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of the
AMERICAN CHEMICAL SOCIETY

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

Rubber Chemistry and Technology may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Division of Rubber Chemistry by payment of the dues ($2.50 per year) to the Division and thus receive Rubber Chemistry and Technology.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Division of Rubber Chemistry upon payment of $5.00 per year to the Treasurer of the Division of Rubber Chemistry, and thus receive Rubber Chemistry and Technology.

(3) Companies and libraries may subscribe to Rubber Chemistry and Technology at a subscription price of $5.00 per year.

To these charges of $2.50 and $5.00, respectively, per year, postage of $.20 per year must be added for subscribers in Canada, and $.50 per year for those in all other countries not United States possessions.

All applications for regular or for associate membership in the Division of Rubber Chemistry with the privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, missing numbers, and all other information or questions should be directed to the Treasurer of the Division of Rubber Chemistry, C. W. Christensen, Monsanto Chemical Company, 1012 Second National Building, Akron, Ohio, or to the Office of Publication, 1500 Greenmount Ave., Baltimore, Maryland.

Articles, including translations and their illustrations, may be reprinted if due credit is given Rubber Chemistry and Technology.

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FALL MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY, ATLANTIC CITY, NEW JERSEY, SEPTEMBER 11-12, 1941

The Division of Rubber Chemistry held its annual Fall Meeting at Atlantic City, September 11 and 12, in conjunction with the One-Hundred-and-Second Convention of the American Chemical Society.

The technical sessions, held in Convention Hall, opened Thursday afternoon with a Symposium on Rubber for Defense. After an introduction by the Chairman, R. H. Gerke, the following papers were presented:

1. Coöperation of the Rubber Industry with Defense. Prepared by W. L. Finger and presented by Richard A. May, both of the Rubber Unit of the Office of Production Management.
2. The Present Status of Crude Rubber. E. G. Holt, Department of Commerce.
3. The Present Status of Synthetic Rubber. E. R. Bridgwater, E. I. du Pont de Nemours & Company.
4. The Present Status of Rubber Chemicals and Reclaimed Rubber. I. P. Coe, Naugatuck Chemical Company.

The interest in these timely papers was great, as was indicated by the unusually fine attendance, which ran as high as 600. The Chairman is to be complimented for his success in securing, in a time of stress such as we are now experiencing, four outstanding representatives of the United States Government and of the rubber industry to participate in this symposium.

It had been planned to open the program with the first Charles Goodyear Lecture. However, Dr. David Spence, whose election as the first recipient of this honor had been announced at the St. Louis Meeting of the Division, was unable to deliver the lecture because of illness.

One of the objects in creating the Charles Goodyear Lectureship is to give recognition to outstanding contributions to the science of rubber. The Executive Committee, wishing to give such recognition to Dr. Spence even when he was

unable to give the lecture, adopted the following resolution, which was announced to the convened membership:

WHEREAS, David Spence was unable because of illness to deliver the first Charles Goodyear Lecture before the Division of Rubber Chemistry at its 1941 Annual Meeting,

Be It Resolved, That David Spence be officially elected the First Charles Goodyear Lecturer, and that a scroll certifying this honor be presented to him by the Charles Goodyear Lecture Committee.

The Divisional banquet, held Thursday evening at the Ambassador Hotel, was a most successful function. Approximately 440 members and guests attended. The Division is indebted to Peter Pinto, Chairman of the Entertainment Committee, and to the members of that Committee for doing an excellent job, and to the following companies for their generous contributions, which made the entertainment possible:

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The program of the Friday sessions was devoted to general papers and to the business meeting. The attendance at these general sessions was excellent, averaging around 400. The program follows:

1. REPORT OF CRUDE RUBBER COMMITTEE. G. A. Sackett.

2. A STATISTICAL STUDY OF THE DETERMINATION OF THE VARIABILITY OF NO. 2 SMOKED SHEET. Hugh M. Smallwood.

3. UNSTABLE ADDITION-COMPOUNDS OF SULFUR WITH ZINC DITHIOCARBAMATES. Ross E. Morris.

4. THE EFFECT OF REINFORCING PIGMENTS ON THE UNSATURATION OF RUBBER HYDROCARBON. F. S. Thornhill and W. R. Smith.

5. BRITTLE POINT OF RUBBER UPON FREEZING. M. L. Selker, G. G. Winspear, and A. R. Kemp.

6. THE EFFECT OF LOW TEMPERATURE ON NEOPRENE VULCANIZATES. F. L. Yerzley and D. F. Fraser.

7. THE ELECTRICAL PROPERTIES OF NEOPRENE. F. L. Yerzley.

8. STATIC ELECTRIC PROBLEMS IN TIRES. E. E. Hanson and J. W. Liska.

9. STATIC ELECTRICITY AND ITS EFFECT ON CAR-RADIO PERFORMANCE. S. M. Cadwell, N. E. Handel, and G. L. Benson.

10. THE EFFECT OF PHOSPHATE-BUFFER MIXTURES ON RATE OF CURE OF CREPE RUBBER. E. B. Newton.

11. AN EVALUATION OF THE BUFFER CAPACITIES OF CERTAIN CRUDE RUBBERS. E. B. Newton and E. A. Wilson.

In the business meeting, held Friday afternoon, H. G. Bimmerman, Chairman of the Tellers Committee, reported the election by letter ballot of the following officers for 1941-1942:

Chairman	John N. Street
Vice-Chairman	John T. Blake
Secretary	H. I. Cramer
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Directors	R. H. Gerke, *ex officio*
	Fred Amon
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	Charles R. Park
	Wm. F. Tuley

The success of the new method of conducting the election of officers by letter ballot was indicated by the fact that the largest number of votes in years was cast, namely 328.

C. R. Haynes, Chairman of the Membership Committee, reported that the membership in the Division was steadily increasing, in spite of the appreciable drop in the number of European members. A summary of the present status of the membership and of subscriptions to *Rubber Chemistry and Technology* follows:

Total membership on August 3, 1941		790
Members	622	
Associate members	168	
New members and associate members from March 31 to August 3, 1941 (included in total membership)		49
Members	33	
Associate members	16	
Subscriptions to *Rubber Chemistry and Technology* (includes 150 to Rubber Manufacturer's Association, but excludes 790 to the general membership)		359
Honorary members and exchange subscriptions		24

Peter Pinto, Chairman of the Entertainment Committee for the Atlantic City meeting, reported an appreciable balance from the banquet, which would be turned over to the Treasurer as a reserve for the use, if required, of the Entertainment Committee for the Memphis meeting. The Chairman congratulated Mr. Pinto and his Committee for their excellent work.

John N. Street, Chairman-elect, announced that it is planned to hold the next meeting of the Division in Memphis, Tennessee, next April, as part of the Spring 1942 Convention of the American Chemical Society. He announced also that plans were already under way for the Fall 1942 meeting, which will be held in Buffalo, New York.

H. I. Cramer, *Secretary.*

NEW BOOKS AND OTHER PUBLICATIONS

Priorities and Defense. Division of Priorities. Office of Production Management. Washington. 69 pages.

A clear explanation of what priorities are and how the system works is presented in this booklet, which also contains the priorities critical list as revised to March 15, 1941, War and Navy department instructions on priorities, copies of preference rating certificates and forms, and other information pertinent to the subject. It is emphasized that one of the most important factors in the whole system is the matter of proper scheduling of production for defense. Thus the armed services can issue preference-rating certificates on the more than 200 items on the critical list to insure priority of production according to the assigned rating.

Certain items of which there is a serious shortage have been subjected to industry-wide control and allocation by the Priorities Division. Neoprene, aluminum, magnesium, and machine tools are examples of the latter class. [From the *India Rubber World*.]

COMMODITY YEAR BOOK. 1941. Commodity Research Bureau, Inc., 82 Beaver St., New York. Cloth, $8\frac{1}{2}$ by $10\frac{7}{8}$ inches, 636 pages. Price $7.50.

This, the third annual volume of a series, contains, in separate sections, discussions of the marketing of 75 different basic commodities, including rubber, followed by charts and statistical data on each material. The presentation of marketing discussions in this volume is in line with the purpose of presenting a different phase of commodities in each edition. It will be recalled that, in the 1940 edition, the discussions were centered on processing methods for converting raw materials to finished form. The section on rubber this year briefly covers: preparation for shipment; baling; transportation; international control; the Rubber Reserve Co.; reclaimed rubber; and synthetic rubber.

In addition to the separate commodity sections, the volume includes three feature articles: "War Time Control of Commodities"; "Economic Functions of Commodity Exchanges"; and "War and Commodity Prices." [From the *India Rubber World*.]

MANUFACTURES—1939, RUBBER PRODUCTS. United States Department of Commerce, Bureau of the Census, Washington. 16 pages. For sale by the Superintendent of Documents. Price 10c.

A comprehensive statistical survey of rubber manufacturing in this country for the years 1939, 1937, and, in some cases, 1929, is detailed in this pamphlet. The phases of manufacturing covered include: number of establishments in the specified branch of rubber manufacturing; number of wage earners and value of wages; cost of materials, supplies, fuel, and purchased electrical energy; value of products; horsepower of prime movers; and rubber consumption. For this survey, the industry is divided into four groups: (1) tire and inner tubes, (2) rubber boots and shoes including rubber-soled shoes with fabric uppers, (3) reclaimed rubber, and (4) rubber products not classified elsewhere. [From the *India Rubber World*.]

INDUSTRIAL PLASTICS. (Second Edition.) Herbert R. Simonds. Pitman Publishing Corp., 2 West 45th St., New York. 6 x 9 in. 385 pp. $4.50.

The publication of this second edition of "Industrial Plastics" so soon after the first is indicative of the rapid progress being made in and with plastics. Like the first, it treats with the derivation, manufacture, use, and possibilities of the wide range of plastics now commercially available. The chapter on "Future of Plastics" has been extended to include a section on "Plastics in Wartime," in which attention is given to the use of plastics in planes and their parts, bomb fins, bulletproof composite plates, submarine battery-holders, machine-gun carriers, cartridge shells, etc.

All tables and statistics have been brought up-to-date in this second edition, and most of the charts have been redrawn to include the latest available information. The chapter on chemistry has been largely rewritten, and many formulas have been revised in the light of recent research. Material has been added concerning types of plastics developed since publication of the first edition, and brief comment is made about new fibers and bristles. Reference to rubber, synthetic rubber and rubberlike materials is made in the chapter on "Other Plastics

and Borderline Materials". Mention is also briefly made of the use of rubber coatings on metal inserts in compression molding.

The book has fifteen chapters in all, the last of which lists the trade name, type and manufacturer of all known plastics, the limits for the list being American plastics, synthetic plastics, commercially active plastics and cold molded materials of plastics type. There is also a comprehensive index. Since the field of utilization for plastics ranges from ash trays to xylophones, this book is a helpful treatise for everyone concerned with plastics, from producer to consumer. [From *The Rubber Age* of New York.]

PLASTICS MOLD DESIGNING. Gordon B. Thayer. American Industrial Publishers, Fairmount-Cedar Building, Cleveland. 6 x 9 in. 64 pp. $2.50.

Not only are the fundamentals of plastics mold design discussed in this book, which is based on material published serially in the *Tool & Die Engineer,* but they are applied to representative types of compression and injection molds. The important compression-mold types are classified and described. Some space is devoted to fixtures, which are an important auxiliary in plastics molding. Mold sinking methods are described, and product design is discussed in relation to mold-building methods. Mold terms are defined in a special section on nomenclature. Pen and ink drawings, all by the author, are liberally used.

The above will give the reader an idea as to the contents of this little book, but it could not convey the value that this "mold handbook" gives to both the mold manufacturer and the plastics molder. Like rubber, most plastics are variable, and molds must be carefully designed, with all variable factors considered, before construction. Would that such a "handbook" on rubber molds were available! [From *The Rubber Age* of New York.]

EMULSIONS AND FOAMS. Sophia Berkman and Gustav Egloff. Reinhold Publishing Corp., 330 W. 42nd St., New York, 1941. Cloth, 6 by 9 inches, 591 pages. Author and subject indices. Price $8.50.

In view of the rapid expansion in the use of latex and in the production of synthetic rubber during recent years, emulsification and foaming are phenomena of increasing significance to the rubber technologist. Besides the production of emulsions and foams, this well-documented book deals with breaking emulsions and preventing undesirable foaming.

The first of the five chapters discusses with some detail the theory of emulsions and foams. Subjects treated by the authors in this chapter include: the relation of surface tension to emulsification; the influence of viscosity on the stability of emulsions; the types of emulsifiers and their functions; hydration, especially with regard to Fischer's theory of emulsification; the significance of volume relations and the influence of such factors as the distance between the globules of the dispersoid on the critical point at which the phases invert; the effects of the electrically charged double-layer of the dispersoid, the dielectric constant, and the presence of electrolytes; particle size in relation to emulsion stability; foam formation and the forces involved in maintaining foam stability; and factors influencing foam prevention.

Descriptions of various laboratory techniques used in the examination of emulsions are detailed in the last chapter; while preceding chapters impart practical knowledge regarding emulsification and demulsification; asphalt and bitumen emulsions and lubricants and lubricating oil emulsions particularly are treated in detail. There are a limited number of brief references to latex and rubber in the text, although no chapter or section is devoted entirely to this subject. Seven

bibliographies are presented throughout the book, and over 600 names are listed in the author index. [From the *India Rubber World*.]

SYMPOSIUM ON COLOR—ITS SPECIFICATION AND USE IN EVALUATING THE APPEARANCE OF MATERIALS. American Society for Testing Materials, 260 So. Broad St., Philadelphia. 6 x 9 in. 86 pp. $1.00, paper cover; $1.25, cloth binding.

Sponsored jointly by the Inter-Society Color Council and the A.S.T.M., this symposium, held at Washington, D. C., March 5, 1941, stresses the importance of adequate specifications for color, and discusses the use of color in the testing and evaluation of materials.

Following the "Introduction to Color" by Deane B. Judd, who covers the attributes of colors, and the distinction between the psychological definition of color and the technical definition, there is a paper on "Color Specifications of Transparent Materials" by Francis Scofield, who reviews critically the various sets of standards. R. H. Sawyer, whose paper covers "Hiding Power and Opacity", discusses the most significant theoretical and empirical relations which have been developed and those practical testing methods which have attained widest recognition.

"Color Standards for Opaque Materials" is the subject of I. H. Godlove's paper, who points out that material standards may vary from haphazard and variable traditional objects which lead to unprecise color names, to groups of standards such as the Ostwald and Munsell systems. The two closing papers deal with the practical problems of color testing, one by A. E. Parker, entitled "Spectrophotometry and Color Evaluation", and the other by R. S. Hunter covering "Photoelectric Tristimulus Colorimetry." [From *The Rubber Age* of New York.]

MECHANICAL VIBRATIONS. (Second Edition.) J. P. Den Hartog. McGraw-Hill Book Co., Inc., 330 W. 42nd St., New York. 1940. Cloth, 6 by 9 inches, 448 pages. Indexed. Price $5.

Although primarily a textbook, this volume has also been written to meet the needs of the practicing engineer. Thus, in addition to covering the theoretical aspects of vibrational phenomena, the book emphasizes the application of principles and calculations to the solution of practical problems in vibration, enabling a rational approach in the design of vibration isolators. [From the *India Rubber World*.]

THE AUTOMOBILE INDUSTRY. E. D. Kennedy. Reynal & Hitchcock, Inc., 386 Fourth Ave., New York. 5½ x 8¼ in. 334 pp. $3.50.

This is a story of the growth of the automobile industry, chronologically told. Although the author is a financial writer and is concerned mainly with the financial side of the industry's growth, it was inevitable that he uncover and incorporate in his story the picturesque and romantic details with which the automobile industry is saturated. It begins with the horseless carriage era of the 1890's and is carried up through the year of 1940, from the beginnings of Hiram Percy Maxim to the death of Walter P. Chrysler, who did much to aid and abet the introduction of mass production methods.

The tremendous growth of the automobile industry is indicated by some of the author's terse comments. For instance, he makes reference to the fact that 50 years ago there was not a single gasoline automobile in the United States; 40 years ago there were about 4,000; today there are some 30,000,000, more or less. As to the manufacturing trend, he points out that once there were scores of active manufacturers, with 700 different makes on record by 1916, but today the different makes can be counted on the fingers of two hands.

Naturally, the role played by several of the larger rubber manufacturers in the growth and development of the automobile industry creeps into Kennedy's story from time to time. For this reason, as well as the fact that the complete story is told in good and easily-assimilated English, "The Automobile Industry" should prove to be interesting reading to members of the rubber industry. [From *The Rubber Age* of New York.]

DANGERS AND HEALTH HAZARDS OF FIRE GASES. Harold Joe Davis. Published by the Author, 3927 East Admiral Place, Tulsa, Oklahoma. 6 x 9 in. 16 pp. 25c.

The purpose of this booklet is to better familiarize those responsible for both industrial and public safety with the dangers and health hazards of fire gases. Lethal fire gases given off during the burning of many combustible materials are discussed. Reference to the burning of rubber is made. [From *The Rubber Age* of New York.]

HANDBOOK OF CHEMISTRY. (Fourth Edition.) Compiled and edited by Norbert A. Lange, assisted by Gordon M. Forker. An appendix of Mathematical Tables and Formulas by Richard S. Burington. Handbook Publishers, Inc., Sandusky, O. 1941. Fabrikoid, $5\frac{3}{8}$ by $7\frac{3}{4}$ inches, 1,935 pages. Indexed. Price $6.

While retaining the general characteristics of previous editions, the present work has been expanded by 85 pages and contains 11 new tables, including four pages of data on synthetic rubbers. One table presenting emission-spectra data has been replaced by two new tables, "Qualitative Spectographic Analysis" and "Sensitive Lines of the Elements". Fifteen tables have been extended or completely rewritten.

The information contained in the new tables on synthetic rubber was taken from "Bureau of Standards Circular C 427, Synthetic Rubbers" by Lawrence A. Wood (1940). The tables are entitled: "Varieties of Synthetic Rubber"; "Chemical Structures of Synthetic Rubbers"; "Electrical Properties of Synthetic Rubbers"; "Physical Properties"; and "Swelling of Vulcanized Synthetic Rubbers in Liquids". [From the *India Rubber World*.]

REPORT OF THE CRUDE RUBBER COMMITTEE

PRESENTED AT THE SEMI-ANNUAL MEETING OF THE DIVISION OF RUBBER CHEMISTRY—APRIL 11, 1941

The Crude Rubber Committee is pleased to present in its report two tests for crude rubber. These tests are subject to criticism and revision, as are other tests proposed by the Committee, and it is earnestly requested that comments or criticism be addressed to the Committee, in which case they will be given serious consideration and study.

The tests proposed have to do with the determination of plasticity and with the property known as water absorption. Both tests can be carried out in any well-equipped rubber laboratory, and their adoption by the Committee does not imply that other methods could not be used, but rather that the Committee felt the methods proposed were quite well known and the equipment is available in a number of laboratories, both in the United States and abroad.

I. Plasticity Test for Crude Rubber

The test described is for crude rubber, and is not proposed as a general plasticity test. Nor is it intended for factory control but, rather, as a test for the purpose of evaluating given samples or lots of crude rubber.

The test is based on the use of known and published methods of determining the degree of plasticity of a sample of crude rubber which has been divided into three identical portions, each portion being masticated to a different degree of softness. The conditions for mastication are described, and also the method of making the actual measurements.

The following method of sampling a bale or case is suggested as very suitable. Cut the package from top to bottom and remove a slice which includes a portion of each sheet or strip of rubber which makes up the bale. From this remove three samples, of 300 grams each, so that each sheet is included in each sample.

The following describes the test in detail. In each case where the sample is referred to, one of the 300-gram portions described above is meant.

A. MILL

Prepare the sample for test by milling on a laboratory mill. As far as possible the mill should conform to the following specifications:

Roll speed when idling	
Front	25 rev. per min.
Back	35 rev. per min.
Distance between flat portion of guides	25 cm. (10 in.)
Roll diameter (each roll)	15 cm. (6 in.)

In reporting the results of a plasticity test on a sample of crude rubber, it is desirable to give the characteristics of the mill used for the preparation of the sample, since wide variations from the standards might confuse the results.

B. MILLING

Adjust the mill opening to 1.016 mm. (0.04 inch) by measuring the thickness of soft lead slugs passed through each side of the mill while rubber is on the

mill. To do this, cut a portion of rubber off the mill to allow the slug to pass through without being imbedded in the rubber. Pass the slug through the mill twice. The rubber should not be too soft. A good grade of smoked sheet milled for 3 to 5 minutes before adjusting the roll-opening is suggested.

Maintain the temperature of the rolls at 46.1° to 54.4° C (115° to 120° F) throughout the milling of the sample. The temperature and rate of flow of the cooling water to do this should be determined beforehand. A good, reliable surface pyrometer should be used to determine the surface temperature of the rolls.

With the mill properly adjusted for opening and the flow of cooling water regulated to maintain the standard temperature, place one of the 300-gram samples on the mill and pass it through the rolls. Gather the sample together, roll it as well as possible, and pass it through the mill, inserting it into the mill lengthwise and adjacent to one of the guides. In this manner pass the sample through the mill a total of 10 times, 5 times adjacent to one guide, and 5 times adjacent to the other.

Following the 10 passes through the rolls, allow the sample to run on the front roll, without cutting, for a period of 3 minutes, timing the period with a stop-watch, clock, or watch with a second-hand.

At the end of the milling period, cut the sample off the mill and roll up. Insert the roll lengthwise into the mill, catch below the rolls, roll again, and pass through the mill once more. As it emerges from the mill the second time, take it off as a sheet and fold to the proper thickness for cutting the test-piece (as described in "C" below). Chill it immediately in tap water at 15.5° to 21.1° C (60°-70° F) for 5 minutes to minimize plasticity changes before testing. Testing must be carried out within 24 hours after the milling.

To determine the plasticity behavior of the sample, three points on a plasticity curve are found. Three points give a much better idea of the behavior of a rubber sample on breaking down on a mill than can be obtained from a single test.

The detailed description above is for the 3-minute point. The other points determined are for 6 and 9 minutes. They are run identical in every way to the point described, except that the periods of running the sample on the front roll are 6 and 9 minutes, respectively.

C. TESTING

Because no single instrument is available in all laboratories, the Crude Rubber Committee suggests two methods of testing, with the idea that at least one will be available in most laboratories where crude rubber testing is carried on. The instruments specified are the Williams plastometer and the Mooney shearing-disc plastometer. As the methods are not similar, it is not possible to transpose the results directly from one test to the other, but considerable investigation has shown that the curves obtained by plotting the results against time of milling are about the same in shape and type.

The following test conditions are prescribed.

1. Williams Plastometer

This method measures the final thickness of a specified volume of rubber after it has been pressed with a given weight for a specified time and at a given temperature.

The test is made at 70° C (158° F). The volume of the pellet is 2 cubic centimeters. The load is exactly 5 kilograms, and the duration of the load is

3 minutes. The final gauge is read in millimeters, and is known as the Williams plasticity index. The pellet is preheated at 70° C for 15 minutes before testing to make sure it is at the standard temperature.

The pellet is cut from the slabs taken from the mill, which have been folded to a thickness of 0.75 inch (1.5 cm.). A cylinder is cut from the slab with a cork borer 14 mm. in diameter. It is trimmed to the exact volume of 2 cc. by cutting the flat ends until the weight of the pellet is exactly 1.84 grams.

During the measurement of plasticity, a piece of cellophane or Holland cloth may be used above and below the sample to prevent adhesion of the rubber to the metal of the instrument. Allowance for the thickness of the material used must always be made.

2. Mooney Shearing-Disc Plastometer

In this test, the rubber is sheared by a rotor driven within a closed chamber by a synchronous motor. The resistance to shear develops a thrust in a floating, horizontal worm shaft, and this in turn deflects a spring so a reading can be made. The deflection of the spring is theoretically proportional to the viscosity of the sample, averaged over a range in rate of shear and expressed in arbitrary units.

The temperature of the test is 100° C (212° F). The sample for testing is in the form of two slabs with minimum dimensions of 5 cm. by 5 cm. by 6 mm. (2 in. by 2 in. by 0.25 in.).

Coat the rotor and the surfaces of the plastometer which come in contact with the rubber with a dilute liquid soap (2-3 per cent solids) by means of a paint brush, and allow to dry. This is to prevent adhesion of rubber to the metal.

Slit one of the slabs of rubber to be tested, and push the shaft of the rotor through the slit. Place the second slab of rubber over the rotor, insert the assembly into the plastometer, and close the chamber, thereby cutting and molding the sample.

Allow one minute for the rubber to come up to temperature and then start the motor which drives the rotor. At the end of 3 minutes, read the gauge, and record as the Mooney plasticity index.

Discussion of the Plasticity Tests

Previously proposed plasticity tests called for but one point on the plasticity curve. As different rubber samples behave differently on milling, the single point is not sufficient to reflect the behavior of the rubber on processing. It is believed that the determination of three points gives the information needed, without sacrifice of any of the good points of other tests proposed, and without excessive time or labor.

The rubber must not be cut on the mill except as specifically stated. The operation of cutting rubber on a mill is a source of great variation, since no two operators cut rubber exactly alike. This leads to a variation which cannot be compensated for, and it is difficult to reproduce runs. It is felt that the method proposed accomplishes satisfactory blending.

The Williams test is specified to be carried out at 70° C, the Mooney test at 100° C. The longer time of heating for the Williams test is apt to induce plasticity changes, due to temperature, if a higher temperature is used. The speed of the Mooney test allows the use of a higher temperature, and experience has shown that 100° C is desirable for satisfactory operation.

The Committee does not believe that the results of a test on the Williams

equipment can be translated into terms of results on the Mooney equipment or *vice versa*. They are widely different tests in every way, and both tests are specified because both are widely known and used. This does not mean that other tests are not equally well known or used, but the selection was influenced by knowledge that equipment for both tests is available in this country and abroad.

The Williams test is sometimes expanded to include a "recovery" figure. This is not a true measure of viscosity of the sample, but of the elasticity retained in it. It is not regarded as a good index of plasticity and, therefore, is not proposed as a part of the standard test.

The tests for plasticity generally measure the mean viscosity of the sample under given conditions. The Crude Rubber Committee suggests that more precise terminology would be viscosity rather than plasticity, and the tests should be so known.

II. Water Absorption Test for Crude Rubber

This test is used to determine the amount of moisture absorbed by a piece of crude rubber of specified dimensions when it is soaked in water at a definite temperature for a given length of time.

The method of sampling suggested is to cut through the bale and remove a slab 1.5 inches thick from the center of the bale or case. A section 2 inches wide is removed from the center of this slab. This gives a cross-sectional plug from the center of the bale, and it contains a portion of each sheet in the package.

A. MILLING

Break down the cross-sectional plug, weighing approximately 800 grams, on a laboratory mill, and blend by giving it 10 endwise passes through a laboratory mill, rolling as well as possible with each pass. After this preliminary blending, the weight of the batch is reduced sufficiently to cover the front roll and leave only a 1 inch rolling bank. Then cut the rubber back and forth continuously for 10 minutes. Finally, allow the rubber to run around the front roll of the mill to obtain a smooth surface, and then remove it.

Maintain the rolls at 70° C (158° F) by a controlled flow of cooling water, and set the opening between the rolls to obtain a finished sheet .070 to .075 inches (.178 cm. to .191 cm.) thick.

Immediately after removing the rubber from the mill, place it between two sheets of aluminum foil and allow it to cool at least 24 hours.

Remove a test-piece with the covering remaining on the rubber, using a 2-inch by 5-inch die (5.08 cm. by 12.70 cm.).

(Note.—The use of cellophane or Holland cloth as a covering is not recommended because substances used in these materials may be absorbed by the rubber and give false water absorption values.)

B. TESTING

Remove the foil and electrically discharge the sample on a grounded metal plate before weighing. Carefully weigh the test-piece to the nearest milligram, and fold a piece of aluminum wire screen about the sample, being careful not to imbed the wire in the rubber. The screen should be about 10 mesh.

Immerse the screen-enclosed sample in distilled water kept at 70° C (158° F), within plus or minus 0.5° C. The period of immersion is 20 hours. On with-

drawal from the water, remove the screen, blot the sample lightly with lintless material, and dry the surface in a stream of air at room temperature for about 5 seconds. Allow the sample to stand 1 minute before weighing in a weighing bottle. Weigh to the nearest milligram. The difference between the original and final weight is the total water absorbed.

c. CALCULATION OF RESULTS

The results should be reported in terms of percentage of water absorbed, based on the original weight of the sample.

Discussion of Water Absorption Test

Some technologists have reported water absorption in terms of milligrams of water absorbed per unit area. If the size of sample used is the same as that recommended above, the results can be approximately calculated to a percentage basis. Because of the effect of the area of the sample on the amount of water absorbed, any results obtained on pieces of dimensions other than those specified cannot be reliably calculated to a comparable basis, either in percentage or absorption per unit area.

The water absorption of crude rubber has been reported frequently as milligrams per unit area. The area chosen has been the square inch. To convert

TABLE I

EFFECT OF DEGREE OF MASTICATION ON PERCENTAGE WATER ABSORPTION OF RUBBER FROM TWO DIFFERENT ESTATES

	Estate A	Estate B
Unmilled Sheet	7.30	5.65
Milled 5 minutes	4.90	3.44
Milled 10 minutes	5.71	3.92
Milled 15 minutes	5.64	3.88
Milled 30 minutes	5.58	4.02

such results to a percentage basis, the original dimensions and weight must be known if the calculation is to be exact. In some cases the area of the edges is included in the calculation; in others it is neglected. On the basis that the area of the sample is 21.02 sq. in. (135.6 sq. cm.), in which case the original weight is 10.98 grams, an approximate conversion to a percentage basis can be made as follows:

$$\% \text{ absorbed} = \frac{\text{mg. per sq. in.} \times 21.02 \times 100}{10980} = \text{mg. per sq. in.} \times 0.191$$

To compare any test results on water absorption, the area exposed, as well as the conditions of test, must be the same in each case. It is hoped that all future tests will use the area and conditions specified above.

Effect of Milling

It has been found that milled crude rubber gives values which correlate better with results on vulcanized compositions than the values obtained from unmilled rubber.

A "dead-milled" rubber is used in the procedure specified by the Crude Rubber Committee, because such rubber does not change in dimensions due to shrinkage, and because it also gives a smooth surface and thus a surface area easily measured. The effect of long milling is shown in Table I.

Sampling

If possible, the whole bale should be well blended on a factory mill, and a sample removed from this. If this is not practical, the bale should be sampled as recommended. Single sheets cannot be tested as representative of the bale. The following tables show the results obtained from single sheets, compared to a blended sample, and a comparison of the results from the recommended sample with the results of the blended bale. Table III shows also the effect of insufficient milling of the sample on the results obtained.

These data show that tests on unmilled sheets selected from a bale are not indicative of values which would be obtained on a blend of a bale.

The result obtained after the 5-minute laboratory milling is low, due to insufficient milling, which permitted a change in dimensions of the sample during the immersion period. Similar results can be observed in the data shown in Table I.

TABLE II

COMPARISON OF SINGLE SHEETS WITH BLENDED BALE

	Estate C, per cent	Estate D, per cent	Estate E, per cent
Top of bale (unmilled sheet)	6.17	10.01	4.88
Middle of bale (unmilled sheet)	8.48	10.57	6.84
Bottom of bale (unmilled sheet)	7.41	10.14	5.97
Blend of bale (milled)	4.66	6.31	3.62

TABLE III

COMPARISON OF FACTORY BLENDED BALE AND CROSS-SECTIONAL SAMPLES

	Percentage water absorption
(1) Factory blend of bale	5.77
(2) Blend of 1.5-inch cross-section of bale	5.73
(3) Blend of 2-inch section of cross-section (2)	
(a) 5 minutes on laboratory mill	4.89
(b) 15 minutes on laboratory mill	5.73

Testing

The aluminum wire screen will be found very useful in supporting the specimens and separating them from each other in the water bath. The size of screen used is approximately 2 inches by 11 inches, and it is folded lengthwise around the sample.

The technique of removing moisture from the surface of the sample after immersion involves the human element. This is also true for the length of time required for weighing. Both have an effect on the result. With a little experience, however, operators acquire a uniform technique and only slight discrepancies are found in duplicate samples.

Data Obtained on Various Lots of 1X Smoked Sheet Rubber

The results given below were obtained from tests of smoked sheet rubber bought on the open market. They do not represent data from samples claimed to have low water absorption properties, and are recorded here merely to show the range of variation between bales from a given estate.

In some cases values of 10 per cent or more have been obtained. It has been observed, however, that single small shipments from a given estate are fairly uniform within themselves, and a test made as recommended on 10 per cent of the packages in the shipment gives a reasonable indication of the characteristics of the entire shipment. It is suggested that separate bales be tested, rather than a blend of the bales.

CONCLUDING REMARKS

The Crude Rubber Committee has not given up the possibility of working out a test for determining the age-resistance properties of crude rubber. Much laboratory work remains to be done on this problem before reaching any decision, and such an investigation will be considerably delayed by the present need for work for national defense.

TABLE IV

WATER ABSORPTION VALUES OF 1X SMOKED SHEET RUBBER

Estate	No. of bales tested	Percentage water absorption
F	16	4.01–4.60
G	6	6.58–7.31
H	8	3.14–3.72
K	20	3.40–4.14

The Committee is giving serious consideration to the problem of sampling crude rubber. The drawing of a representative sample presents more of a practical statistical problem than one of rubber technology, and the adoption of a standard method must be based on a statistical study. It is hoped that a paper on this subject can be presented before the Division of Rubber Chemistry at an early date.

ACKNOWLEDGMENT

The Committee wishes to acknowledge its indebtedness to A. R. Kemp of the Bell Telephone Laboratories for his assistance in the development of the plasticity test, and its indebtedness to the V. L. Smithers Laboratories for information obtained from their very complete study of plasticity testing.

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RATIONAL PROCESSING *

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INTRODUCTION

The processes to which rubber is subjected before vulcanization depend largely for their success on the raw material being rendered plastic. At ordinary temperatures smoked sheet is an elastic substance having nerve and incapable of being kneaded, extruded or moulded. To facilitate these processes and compounding with fillers, rubber is masticated, either on a two-roll mill or in an internal mixer. Experience has shown that mechanical working reduces the elasticity and nerve of rubber and renders it plastic. Mastication is such a familiar practice in rubber technology that it is taken for granted as the first essential in rubber manufacture. This is unfortunate, because it is costly and has several disadvantages. These will be considered in detail and other means of achieving the same end suggested.

I. PEAK LOAD: THE FREEZING OF RUBBER

During the first few minutes of mastication, the load on the mill or mixer is much in excess of that during the remaining period of mastication. When electrical energy is purchased on the maximum demand system, this constitutes a grave disadvantage; the consumer is severely penalized for putting a strain on the electrical supply for a short period. From the point of view of the supply corporations, this is inevitable, because they must be ready to supply current much in excess of normal for a short period after the rubber works open in the morning.

When smoked sheet and crepe rubber have been in storage for some time, they gradually harden and assume a frozen condition. This is due to crystallization of one or more of the hydrocarbon components of the rubber. When this board-hard rubber is placed on the mill, not only does its physical condition impose a severe load on the machine, but before it can begin to soften, the mill must supply the latent heat required to melt the frozen components of the rubber. This heat may be conducted from the hot roll or be produced by internal friction within the rubber.

The melting point of normally-frozen smoked sheet rubber is between 31.5° and 33° C, although van Rossem and Loticius[1] have claimed that after storage for 13 years the melting point may rise to 35° to 37° C, and Whitby[2] instances unsmoked sheet made in 1905 which thawed at 43.5° C after 30 years' storage.

It is obvious that, to prevent undue strain on machinery and to keep down the peak load, frozen raw rubber should be warmed to about 40° C before milling.

It is remarkable that, once frozen smoked sheet rubber has been thawed, it is difficult to get it back to the same board-hard condition at ordinary temperatures. If placed in a refrigerator, the rubber will harden and become opaque in a few hours, but will be found subsequently to soften at a temperature of 8° to 10° C, far below that required to thaw it originally. Even after storing for months in a refrigerator at about 0° C, the same conditions prevail, and the artificially frozen

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rubber softens and becomes translucent almost immediately it is exposed to room temperatures. van Rossem and Loticius[1] believe that the lower melting point of the refrozen rubber is due to the smaller size of the crystals compared with those grown in the original stored rubber, but this is an unsatisfactory explanation of the phenomenon.

When masticated rubber is placed in a refrigerator at 0° C, it also rapidly hardens, but will subsequently thaw below 10° C, with absorption of little latent heat. A curious observation, apparently hitherto not reported, is that at normal temperatures masticated rubber hardens in storage more rapidly and completely than raw rubber. Furthermore, the greater the extent of mastication, the harder the rubber eventually becomes. It is intended to investigate this phenomenon more closely. There is reason to believe that it may prove of significance in explaining why mixed rubber stocks, in which the rubber components must often be seriously broken down, harden on storage. This freezing or setting of compounded rubber stocks has in the past been a prolific cause of mill breakages.

It seems probable that rubber can exist in at least two allotropic modifications, having different melting points, and that mastication has a profound influence on the properties of at least one of these.

II. MASTICATION

The softening which rubber undergoes during mastication is mainly the result of a shortening of the average length of the rubber molecules, induced by oxidative rupture. The appreciable regain in nerve on subsequent standing is evidence that disaggregation of molecular assemblages also occurs during mastication, as these might be expected to reform spontaneously.

As oxygen plays an important role in softening rubber during milling, it was natural that attempts should be made to find catalysts capable of accelerating the action. During the past four years numbers have been reported, including phenylhydrazine and its double salts, thionaphthols, xylylmercaptan, *p*-thiocresol, and several proprietary materials. It has also been shown that certain accelerators, in particular 2-mercaptobenzothiazole, act at high temperatures as mastication accelerators. The use of these catalytic agents, frequently, though probably erroneously, termed peptizing agents, does not in the ordinary way reduce the initial load on the mill when masticating rubber, and it is conceivable that their continued action throughout the incorporation of compounding ingredients may result in an undesirable degradation of the rubber substance. The hitherto unattainable tensile strength and excellent aging properties of goods made of rubber direct from latex are evidence that mastication of rubber invariably lowers the standard of the vulcanized product.

If it is practicable to process rubber without preliminary mastication, advantages might be expected.

III. THERMAL PLASTICIZATION

Recent phenomenal development in the moulding of synthetic resins has emphasized that many substances assume a plastic condition within a limited temperature range. This is particularly noticeable with polyphase colloidal systems, such as highly polymerized resins and esters, but also occurs with glass and metals. The former is plastic at about 400° C, and iron can be forged at 700° C. Raw rubber becomes somewhat plastic within the temperature range experienced on mill and calender, but at these temperatures it retains so great

a capacity for elastic recovery that sheeting, extruding and even mixing are impossible. It is strange that little attention appears to have been paid to the plastic properties of rubber at temperatures above 100° C. Admittedly, Ungar and Schidrowitz[3] have softened rubber by heating crumbled rubber in air; but this is essentially an oxidation process which, although showing some advantages over mastication, does not claim to give such a high-quality vulcanized product as would result if the preliminary softening could be eliminated.

If raw rubber could be worked at a sufficiently high temperature, it should exhibit, without preliminary treatment, the plasticity enabling normal processes in rubber technology to be carried out satisfactorily. To investigate this possibility, small discs were cut from a sheet of smoked rubber by means of a Schopper punch. These discs were weighed and made into sets of equal weight, having therefore equal volumes. Discs from a particular set were then subjected to a definite pressure, at temperatures up to 170° C, between parallel plates in a steam-heated hydraulic vulcanizing press employed as a plastometer. Before deformation of the rubber, the tinned iron plates applying the pressure were dusted with talc and raised to the temperature of the press. A disc of rubber was then quickly inserted, and exposed to the full pressure available from the hydraulic accumulator, for a period of three minutes. The plates were then quickly removed from the press and separated, when the diameter of the disc to which the rubber had been pressed out could readily be measured from the mark left by the talc, even though the rubber began immediately to shrink. The area of this disc, divided into the total load on the press, gave an approximate measure of the minimum force per unit area required to deform the rubber at that temperature. This gave a convenient indication of plasticity.

The rubber disc was then stripped from the plate, dusted with talc, and allowed to shrink for five minutes in an oven at 100° C. The surface area after shrinking gave, by difference, a measure of the elastic recovery to which the rubber was prone after deformation at the elevated temperature. It was noticed that the periphery of the recovered disc always remained longer than the circumference of a circle of equal radius, and developed a kink[4] indicative of greater radial grain effect than around its edge. It was further remarked that slow shrinkage continued for some days after the oven treatment.

Results of a typical set of plasticity and recovery readings have been plotted in Figure 1. Plasticity is indicated in terms of the square of the diameter of the extended disc (proportional to its area) under a load of 1 ton per square inch of ram section (ram=3.5 in. diameter).

At 170° C, raw rubber is sufficiently plastic to sheet, as clearly indicated in the accompanying drawing (Figure 2) of a series of discs of smoked sheet subjected to the treatment described. Each extended disc is surrounded by a ring, the external diameter of which is identical with that the rubber acquired under pressure at the corresponding temperature. The recovered discs have the diameter reached after five minutes at 100° C, followed by over a month at room temperature. The results suggested that, at elevated temperatures, smoked sheet might be expected to show even less elastic recovery than experienced with high-quality rubber stocks made in the orthodox way and calendered below 100° C. By extrapolating the graphs relating temperature with plasticity and elastic recovery to a temperature of 200° C (which it is known rubber will withstand without decomposition), it may be predicted that at such temperature rubber approaches perfect plasticity and shows little elastic recovery.

As facilities available did not permit of attaining temperatures above 170° C in the hydraulic press, the simple apparatus illustrated in Figure 3 was devised

to investigate qualitatively the plastic properties of rubber at higher temperatures. A steel bar of rectangular cross-section, 2 feet long, was supported near each end on feet from which it was insulated by means of asbestos washers. At intervals along the rod holes were drilled to accommodate small pools of mercury or molten lead in which thermometers were inserted. The rod was heated at one end by means of a Bunsen burner, and heat was allowed to travel by conduction towards the other end of the rod. After a time a condition of equilibrium was reached, and the temperature indicated on each thermometer was plotted as a graph (Figure 4) against its distance from the heat source. By this means the temperature at any given point along the surface of the bar could be gauged. The stirrup illustrated in Figure 3 was used to press glass microscope slides on to small pellets of rubber by means of a predetermined weight. These little pieces

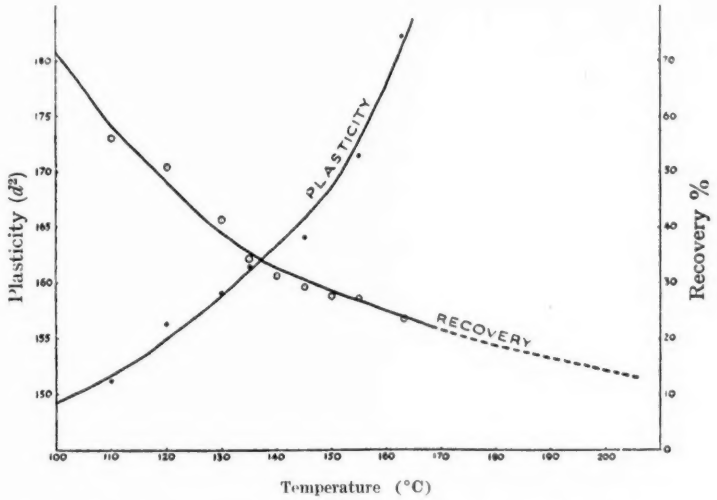

FIG. 1.—Effect of temperature on plasticity and recovery of smoked sheet rubber.

of rubber were cut from smoked sheet by a punch, and had a mean weight of 0.026 gram. The diameter of the discs to which they were deformed after 3 minutes under pressure could be measured through the glass of the slides, and the condition of the rubber, *e.g.*, whether beginning to decompose, could be observed through the slide as a window. The results of a series of tests with this instrument are given in Table I.

The results in Table I and three other similar series of results, have been plotted in Figure 5, on which a curve has been drawn to show the approximate relation indicated between temperature and plasticity of smoked sheet above 170° C. The graph is of the same type as that shown in Figure 1 relating to temperatures between 100° and 170° C. Signs of incipient decomposition were visible above 250° C at which temperature an oily ring on the glass around the edge of the deformed discs indicated commencement of destructive distillation. Nearing 270° C, blisters of vapor developed in the expanding rubber discs.

Up to 250° C, the plasticity of raw rubber rises with increasing rate, without appreciable decomposition occurring.

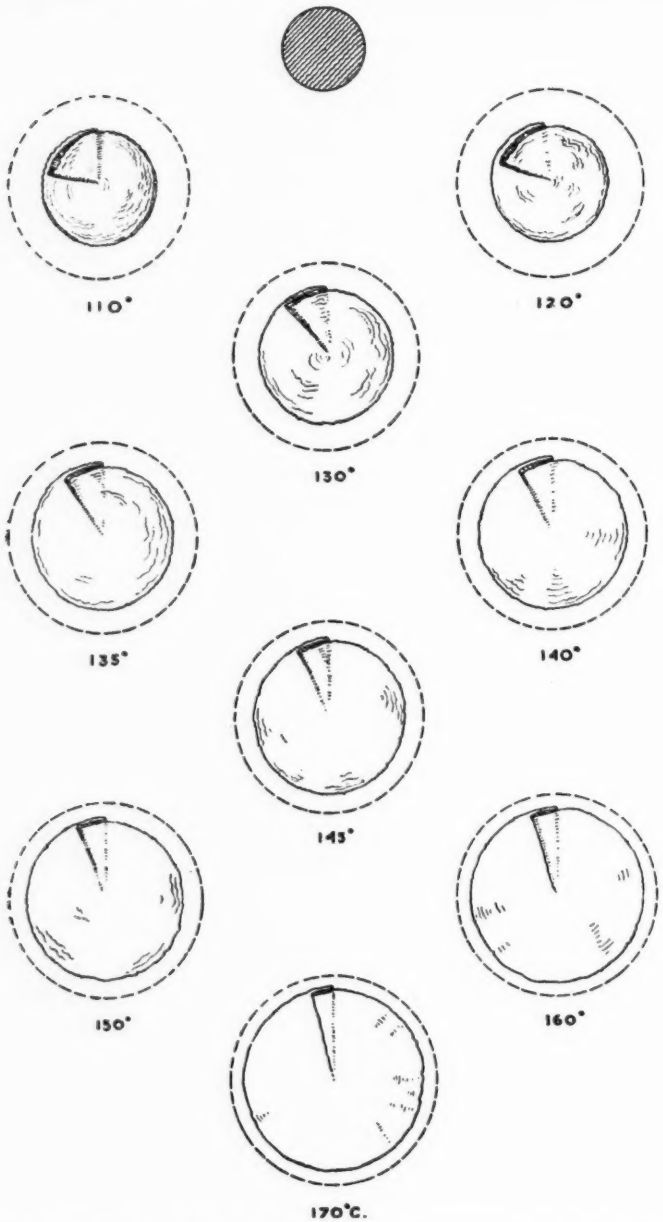

FIG. 2.—Discs of smoked sheet rubber pressed at different temperatures and allowed to recover.

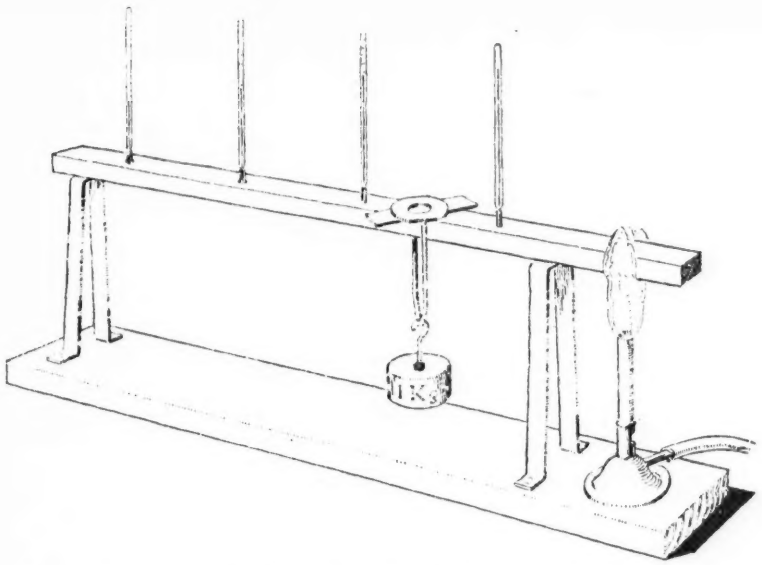

FIG. 3.—Apparatus for determining plasticity of rubber at temperatures above 170° C.

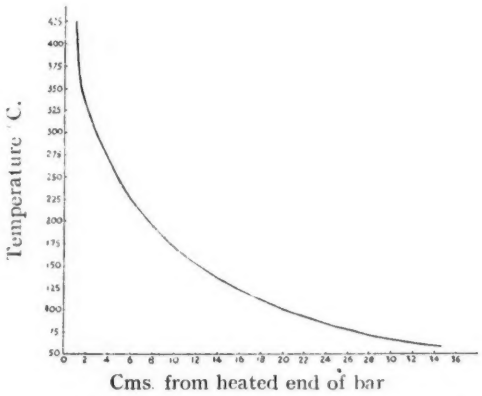

FIG. 4.—Temperature and distance from heat source with apparatus in Figure 3.

TABLE I

Distance from heat source (cm.)	Temperature (°C)	Diameter of pressed disc in cm. (d)	Plasticity Index (d^2)
8	194	1.0	1.0
7.2	205	1.1	1.21
6.5	215	1.15	1.32
5.9	224	1.2	1.44
5.4	232	1.22	1.49
4.85	242.5	1.35	1.82
4.35	255	1.5	2.25
4.0	263	1.6	2.56

IV. UNIFORM HEATING OF RUBBER

A serious drawback to processing raw rubber at high temperatures is the difficulty of heating masses uniformly throughout. The thermal conductivity and diffusivity of rubber are phenomenally low. Possible solutions of the problem include gradual heating of large masses of rubber, as practised in the familiar slow-rise cure; Leduc's process, in which the rubber is employed as dielectric between two electrodes applying a high frequency field, which heats the rubber by electrical hysteresis; and rapid heating of small masses of powdered rubber subsequently compacted while hot.

One of the simplest and most efficient methods of rapidly heating large masses of rubber is undoubtedly by internal friction. It is usual to pass cold water

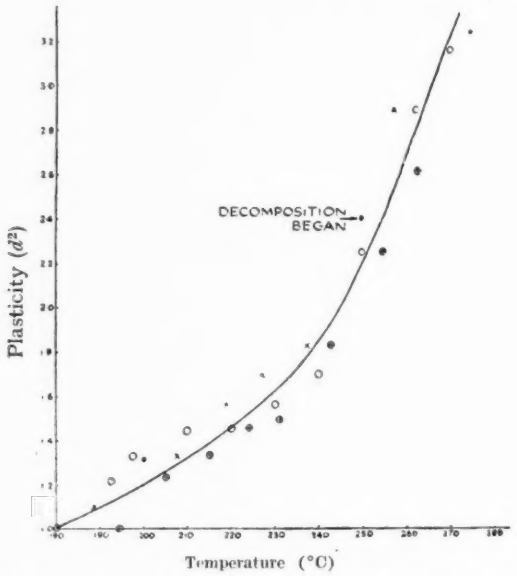

FIG. 5.—Relation between temperature and plasticity of smoked sheet rubber above 170° C.

through mastication- and mixing-rolls, and to spray-cool internal mixers; but apart from a desire to obviate prevulcanization of stocks containing sulfur, there would appear no reason why rubber should not be allowed to attain as high a temperature as it will during these operations. At temperatures between 120° and 200° C, not only is raw rubber naturally thermoplastic, but oxygen attack is more rapid than at normal temperatures, probably 2.5 times as intense for every 10°-C rise in temperature. Hence permanent softening can be achieved in a few minutes. The power consumption involved falls far below that conventionally associated with mastication and mixing.

V. CATALYTIC SOFTENING OF POWDERED RUBBER

Six years ago a Japanese worker, Shimada[5], noted that some organic accelerators of vulcanization have the peculiar property of reducing the viscosity of rubber solutions. He suggested that diphenylguanidine, which reduces solution viscosity at once, is capable of effecting disaggregation of rubber, whereas mercapto-

benzothiazole, which brings about a progressive fall in viscosity, causes depolymerization. These observations led my colleagues R. W. West and P. A. Gibbons (unpublished work) to investigate whether the action was confined to rubber solutions, or could be brought about with dry rubber. For this purpose they dipped strips of pale crepe in alcoholic solutions of various accelerators and other organic chemicals, dried off the solvents, and subsequently exposed to heat in a water oven. Phenomenal softening of some of the treated rubber samples was observed; notably with diphenylguanidine and mercaptobenzthiazole.

TABLE II

EFFECT OF HEATING RUBBER POWDER IN AIR, IN PRESENCE OF CATALYSTS

Addition	Condition after treating in air oven at 90° C for 1 hour	4 hours	24 hours
None	Unchanged	Little changed	Very slight darkening
0.5% phenylhydrazine	Darkening	Softening	—
5.0% phenylhydrazine	[Became too sticky in ball mill to proceed further]		
0.5% diphenylguanidine	No change apparent	Softening	Treacly
5.0% diphenylguanidine	Darker	Soft and dark	Dark brown: very soft
0.5% mercaptobenzothiazole	No change apparent	Softened most	Treacly
5.0% mercaptobenzothiazole	Slightly darker	Soft and dark	Not quite so soft as above
0.5% benzothiazyldisulfide	No change apparent	Softening slightly	Going treacly
5.0% benzothiazyldisulfide	Darker	Darkening	Treacly
0.5% tetramethylthiuram disulfide	No change apparent	Unchanged	Darkening
5.0% tetramethylthiuram disulfide	No change apparent	Unchanged	Browning
0.5% zinc diethyldithiocarbamate	No change apparent	Unchanged	Like control
5.0% zinc diethyldithiocarbamate	No change apparent	Unchanged	Slight darkening

These experiments were recalled by the writer when working with powdered rubber, and it was natural to question what might happen when an intimate mixture of powdered rubber[6] and accelerators in powder form were subjected to heat. Mixes of powdered rubber with various organic chemicals, including phenylhydrazine as a recognized catalytic peptizing agent, were prepared in porcelain mills, placed in glass test-tubes, and hung in an electrically heated oven maintained at 90° C. The results are indicated in Table II. It was noted that mixes containing 5 per cent mercaptobenzothiazole and 5 per cent diphenylguanidine, respectively, acquired sufficient softness to become slightly self-adhesive during ball-milling alone. 0.5 per cent of phenylhydrazine caused appreciable softening during preliminary ball-milling, and a mix with 5 per cent of phenylhydrazine became too soft and sticky to remove easily from the porcelain balls.

Samples containing phenylhydrazine, diphenylguanidine and mercaptobenzothiazole rapidly softened and eventually turned to viscous liquids. In this final condition, the materials had the characteristic smell associated with oxidized rubber, and it is believed that the softening in each case was a direct result of accelerated oxidation, despite the fact that phenylhydrazine might be expected to exert a powerful reducing action. It may be recalled that the theory of antioxidant action propounded by Moureu and Dufraisse predicts that antioxygenic substances may behave as proöxygens under suitable circumstances. It is known that high local concentration of rubber antioxidants may hasten perishing. Blake and Bruce[8] were surprised to observe that materials recognized as antioxidants in vulcanized rubber proved to be among the most effective reagents in accelerating the development of tackiness in unvulcanized rubber in the presence of light.

Samples of the softened powdered rubber were mixed, with sulfur, zinc oxide and, if necessary, additional accelerator, in a mortar with a pestle, and vulcanized in ring-moulds in a hydraulic press. The results were so pleasing that it was decided to make a few test-compounds by ball-milling a mixture of raw powdered rubber, accelerator, zinc oxide, etc., but not sulfur, and to subject them to heat treatment in the hope that the rubber would soften sufficiently to facilitate a perfect cohesion during subsequent moulding and vulcanization. Many previous experiments had shown the futility of trying to produce a strong moulding by compressing a mixture of untreated powdered rubber and fillers.

Preliminary experiments were encouraging. Others are referred to in the latter part of the next section.

VI. RATIONAL COMPOUNDING

The intractable resilient nature of raw rubber at normal temperatures has hitherto made mastication a necessary preliminary to compounding. Subsequent addition of fillers on a mixing mill or in internal mixer must involve further severe breakdown of the rubber. It is probable that increased internal friction consequent on the addition of powders to rubber intensifies the influence of mechanical kneading on the physical properties of the rubber substance. Although elasticity and strength are reimparted by vulcanization, this degradation of the raw rubber must leave its mark on the finished product. Any means whereby the time required to incorporate fillers may be reduced is, therefore, worthy of investigation.

Herein lies one of the advantages of the internal mixer over the two-roll mill. Much has already been done by scientific design of the rotors in internal mixers; but a revolution in mixing procedure might follow a careful investigation of the mechanism whereby filler particles disperse in rubber.

Those conversant with the operation of compounding on a two-roll mill will appreciate the wide divergence between the ease with which different fillers go into rubber. It will also have been remarked that it frequently takes as long to add the last few pounds of powder as the first fifty or more. This was doubtless one of the reasons for introducing the mill apron.

Difficulty experienced in incorporating the last fraction of a mix suggested a series of experiments in which masticated smoked sheet on a pair of 12-by-6 inch mills running at friction speed was compounded as quickly as possible with appropriate volumes of various common fillers, weighing the unabsorbed residue at frequent intervals until none was left. The results are plotted in Figures 6 and 7. During the early stages of mixing, the amount of filler incorporated is proportional to the time of milling; but thereafter the rate of incorporation

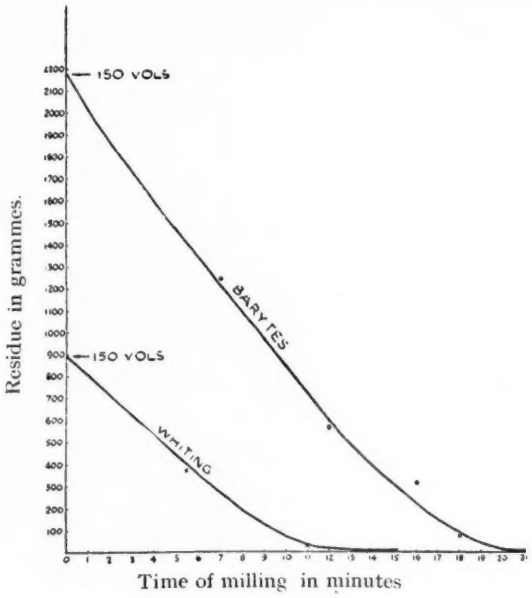
150 VOLS
BARYTES
150 VOLS
WHITING
Residue in grammes.
Time of milling in minutes

FIG. 6.

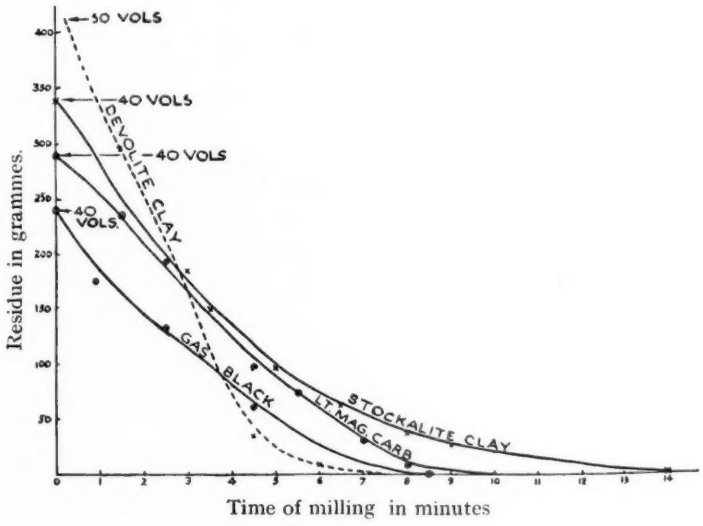
50 VOLS
40 VOLS
DEVOLITE CLAY
40 VOLS
40 VOLS
GAS BLACK
STOCKALITE CLAY
LT. MAG CARB
Residue in grammes.
Time of milling in minutes

FIG. 7.

falls to an extent largely dependent on the physical condition of the filler concerned. Barytes, with large filler particles, mixes easily and quickly throughout, whereas with light magnesium carbonate, Stockalite clay and gas black of small particle size and huge surface area, the rate of absorption falls markedly.

Consideration of these results suggested a new technique of mill mixing, which has proved advantageous. The minor ingredients such as accelerator, antioxidant, zinc oxide and stearic acid, excluding sulfur, are incorporated early in the mix, followed by the powder (whiting, clay, gas black, etc.) constituting the major filler. This is weighed out in predetermined excess, and mixing proceeds as rapidly as possible until the residue in the pan below the mill equals the known excess. This may conveniently be the quantity required to fill a handy scoop. By this simple procedure, time is saved, with corresponding reduction in breakdown of the rubber component. The scoopful of excess filler can be added to the next mix and the process repeated; it is not necessary again to adjust the formula weighed out. The final mixing and blending is coincident with the incorporation of sulfur, always readily absorbed because of its solubility in hot rubber.

Care must be exercised in employing this technique with mixed fillers, because the composition of the residue may change as milling proceeds, owing to the differential absorptive capacity of rubber for the powders. With this reservation, the new technique can save up to a third of the normal mixing time.

The most rational method of compounding rubber might appear to be by addition of fillers as a water dispersion to latex on the plantation, before coagulation; but such unorthodox procedure is not likely to appeal to rubber manufacturers, who wish to see what goes into their compounds. A few experiments have, however, been made along these lines, during which it was surprising to find that the dispersed compounds, particularly gas black, were not wholly precipitated at the *p*H necessary to coagulate the rubber. It had been anticipated that filler and rubber particles would automatically cohere at the isoelectric point of the latter; but this is not necessarily so. With a gas black dispersion, the serum remained almost as black as India ink, and further carbon was removed when the coagulum was washed. The gas black had been dispersed with the aid of Darvan.

Cotton and Hodson[8] made experiments with a view to mixing and moulding rubber without mastication. The compounds were made by ball-milling rubber powder with fillers; but cohesion during subsequent moulding and vulcanization was poor. Observations reported in the preceding section engendered the hope that powdered rubber heat-softened in presence of catalysts, such as phenylhydrazine and diphenylguanidine, might amalgamate with fillers more readily. This was tried with considerable success. The following mixes were made in a ball mill, using but a small fraction of the energy which would have been required to masticate and mix the rubber by conventional means. The sulfur indicated in brackets at the end of each mix was not added until after ball-milling and subsequent heat treatment, when it was incorporated, with as little working as possible, on a two-roll mill.

Pure-gum type mixes.

1A		1B		1C	
Rubber powder	100	Rubber powder	100	Rubber powder	100
Mercaptobenzothiazole	0.5	Diphenylguanidine	0.5	Zinc diethyldithiocarbamate	0.25
Zinc oxide	5	Zinc oxide	5	Phenylhydrazine	0.5
Stearic acid flake	1			Zinc oxide	5
Sulfur	3	Sulfur	3	Sulfur	2

Gas Black mixes.

2A		2B		2C	
Rubber powder	100	Rubber powder	100	Rubber powder	100
Mercaptobenzothiazole	1	Diphenylguanidine	1.5	Zinc diethyldithiocarbamate	0.5
Zinc oxide	5	Zinc oxide	5	Phenylhydrazine	0.5
Stearic acid flake	3	Gas black	40	Zinc oxide	5
Gas black	40			Gas black	40
Sulfur	3	Sulfur	4	Sulfur	2.5

These homogenized compounds were placed in beakers in an oven at 90° C. It soon became obvious that the rubber in most instances was softening. The powders lost their dry feeling, and acquired the capacity to cohere under finger pressure.

An indication of the relative rates at which the mixes softened may be gained from observations made during the experiment, and reported in Table III. It is emphasized that the rubber particles were of necessity seriously oxidized before a marked change in appearance and consistency of the gas black mixes occurred. These contained much dry powder to mask early signs of softening.

The speed with which some of the mixes containing zinc oxide softened under the influence of heat may be significant, in view of the known capacity of zinc oxide for activating the acceleration of vulcanization in the presence of these organic compounds. There may be a parallel between the action of sulfur and oxygen on rubber.

Samples of the compounded and softened powdered rubber were rapidly mixed with sulfur on a mill, and vulcanized in Schopper ring moulds between tinned plates. In some instances it was found necessary to add additional accelerator, as that originally present had lost its potency during the softening process; but the results were sufficiently encouraging to warrant later amplification (see Table IV).

VII. UNIFORM RAPID VULCANIZATION

Hot vulcanization, the last major process to which moulded rubber goods are subjected, invites fundamental reform. Recent research has demonstrated that vulcanization with sulfur in low proportions involves little heat interchange. The enormous amount of steam heat yearly employed in curing rubber serves merely to speed up a chemical union which is, in fact, slightly exothermic. Here is scope for far-reaching economies.

Until the fastest ultra-accelerators can be sufficiently delayed in action to allow of mill-mixing, high temperature vulcanization will remain essential. One of the chief difficulties in this process is the time of heating necessitated by the low thermal diffusivity of rubber. Slow rises or stepped cures have to be given to ensure that the outer layers of large masses of rubber shall not be seriously over-vulcanized before those in the center are cured.

Leduc has achieved uniform temperature rise by employing the rubber as a dielectric between two plates subjected to a high frequency oscillatory electric potential. Unfortunately this involves expensive and dangerous apparatus. Another method of obtaining more uniform rise in temperature in a mass of rubber is to increase its thermal conductivity. This may be done, according to Jones[9], by incorporating aluminum powder, which not only improves cure by assisting heat transfer, but makes such articles as moulded bathing caps more

TABLE III

Mix	Hours of Heating at 90° C. 1.25	3.5	4.75	25.25	94.5	120
1A			Consolidated at bottom.	Sticky at bottom; spongy above.	Easily consolidated by hand pressure.	Becoming treacly at bottom. *Removed.*
1B	Slightly sticky.	Treacly. *Removed.*				
1C	Becoming sticky.	Very sticky; spongy consistency. *Removed.*				
2A			Agglomerating slightly at bottom.	Particles further uniting at bottom.	Little apparent further change.	Easily compressed to solid lump. *Removed.*
2B			Agglomerating at bottom.	Consolidating at bottom.	Top layers becoming spongy; could be consolidated by finger pressure.	Very easily consolidated. Softer than 2A and 2C. *Removed.*
2C			Agglomerating slightly at bottom.	Particles further uniting at bottom.	Little apparent further change.	Easily compressed to solid lump. *Removed.*

TABLE IV

Mix	Type	Softening catalyst	Cure	Moulded: Stress at 400% elongation (lbs. per sq. in.)	Moulded: Tensile strength (lbs. per sq. in.)	Moulded: Elongation at break (Percentage)	Injected: Stress at 400% elongation (lbs. per sq. in.)	Injected: Tensile strength (lbs. per sq. in.)	Injected: Elongation at break (Percentage)
1A	Pure gum	Mercaptobenzothiazole	25* min. at 134° C	190	435	646	—	—	—
1A + 0.5 parts mercaptobenzothiazole	Pure gum	Mercaptobenzothiazole	10* min. at 141° C	516	1410	607	385	1598	699
1B	Pure gum	Diphenylguanidine	30* min. at 141° C	312	1085	694	—	—	—
1B + 0.5 parts diphenylguanidine	Pure gum	Diphenylguanidine	15* min. at 141° C	411	1579	687	366	1235	671
1C	Pure gum	Phenylhydrazine	15* min. at 134° C	164	288	552	—	—	—
1C + 0.25 parts Zinc diethyldithiocarbamate	Pure gum	Phenylhydrazine	5 min. at 134° C	485	1470	608	745	2323	618
2A	Gas black (20 vols.)	Mercaptobenzothiazole	34* min. at 134° C	—	546	308	—	—	—
2A + 1.0 parts mercaptobenzothiazole	Gas black (20 vols.)	Mercaptobenzothiazole	10 min. at 141° C	—	1165	324	1600	2400	638
2B + 1.5 parts diphenylguanidine	Gas black (20 vols.)	Diphenylguanidine	15 min. at 141° C	2087	2183	490	1612†	1848	448
2C + 0.5 parts Zinc diethyldithiocarbamate	Gas black (20 vols.)	Phenylhydrazine	10 min. at 141° C	--	426†	170	1888	1982	418

* Vulcanized samples eventually bloomed sulfur. † Faulty test-ring.

durable. A brief investigation of the effect of aluminum powder in vulcanized rubber has been made by Guppy[10].

Rapid developments in the injection moulding of plastics led the author and Hodson[8] to attempt the production of rubber mouldings from compounded rubber powder by this method. In early experiments with normal moulding, it was noticed that the spew exhibited excellent cohesion. When powdered mixes were forced under great pressure through a small orifice into a heated mould, the individual rubber particles seemed to be partially ruptured, thereby facilitating cohesion. Frictional stresses imposed on the rubber passing rapidly through the orifice produced heat which helped to raise the mix to the vulcanizing temperature and to ensure rapid uniform cure.

As it was possible to soften powdered rubber mixes by heat treatment in the presence of catalysts, it was decided to inject some of the compounds under

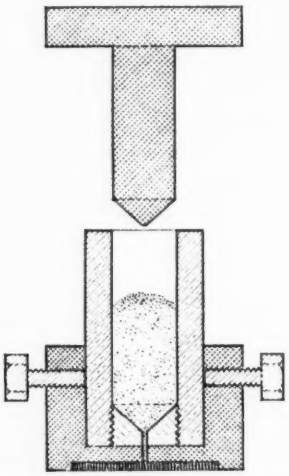

FIG. 8.—Injection mould for rubber powder mixes.

pressure into the mould used in earlier experiments, and illustrated in Figure 8. Homogeneous vulcanized rubber discs, showing no tendency to subsequent distortion, were injection-moulded with greater ease than when employing untreated powdered rubber made by the Stam process. The mixes given in Section VI were used, after ball-milling, heating at 90° C for the times mentioned in Table III, and mixing rapidly with sulfur on a mill. Tensile tests on rings cut from the injected discs are given in Table IV, and compared with those on rings cut from Schopper discs moulded in the orthodox manner in a steam-heated hydraulic press. The state of cure attained in the injected discs was not necessarily identical with that of the corresponding moulded discs, because only one face of the injection mould contacted with the press platen. Furthermore, the size of the injection mould necessitated employing a press which did not happen to be fitted with automatic temperature control like that used for curing the Schopper discs.

There was abundant evidence that the process of injection served to homogenize and consolidate the compounded, softened powdered rubbers. Additional accelerator was found necessary to obtain satisfactory vulcanization: that employed in softening the rubber initially was in every instance partially decomposed. Several

of the vulcanized discs subsequently bloomed (see Table IV), and it is realized that the cures given were not well chosen.

It is believed that more satisfactory results would have been obtained had the rubber powder mixes been less drastically softened. The rubber hydrocarbon in several instances was seriously degraded by oxidation; yet the vulcanized products were of fair quality.

With an efficient delayed-action accelerator, there appears no reason why the injection process should not be employed for moulding and vulcanizing rubber stocks made in the orthodox way. The simplest and most efficient method now known whereby to raise the temperature of a mass of rubber uniformly is by internal friction. With the development of efficient delayed-action accelerators, it may become practicable to allow the temperature to build up on the mill, and then quickly inject the rubber at vulcanizing temperature to the mould. Even if the rubber does not reach vulcanizing temperature in mixing, it is foreseen that the final heat required may be produced by friction in an extruding machine designed continuously to inject the hot stock into moulds. It is even conceivable that the subsequent vulcanization of bulky rubber articles might be achieved by placing the moulds full of hot rubber in a modern prototype of the hay-box, thereby doing away with the necessity for steam in the curing shop.

VIII. MOULDING VULCANIZED RUBBER

Carrying the suggestions of the last paragraph to their logical conclusion, one may speculate on the possibility of moulding rubber articles direct from vulcanized rubber in powder form. The fact that raw rubber becomes thoroughly plastic at temperatures between 200° and 260° C, coupled with the knowledge that similar products in other fields assume plastic properties within a range of temperatures, narrow or wide, led the author to remould ground vulcanized rubber compounds at high temperatures. The highest temperature obtainable by steam in the laboratory available was 175° C; but it was astonishing to find to what extent ground scrap will cohere under pressure at this temperature. It is believed that rubber heels have been made of waste rubber by this process in Spain, and it is confidently asserted that when higher temperatures are attainable in a platen press, *e.g.*, by use of electric heating elements, high pressure steam, diphenyl or other heating medium, it will be discovered that at some temperature just below 260° C, vulcanized rubber will acquire sufficient plasticity to mould readily under pressure, without exhibiting elastic recovery or undue decomposition.

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RUBBER AND ARTIFICIAL RESINS AS "LIQUIDS WITH FIXED STRUCTURES" *

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INTRODUCTION

Numerous investigations, particularly in recent years, have served to throw much light on the relation between the inner structure and mechanical properties of artificial substances. The rapidly developing, industrial production of artificial materials has given considerable impetus to these investigations, since, as has often been pointed out[1], the solid state of organic materials represents the practical and usable form of artificial products. Basing his opinion on the fundamental researches of Tammann, Jenckel has classified many artificial substances as glasses; Houwink and others have seen in colloidal structures certain fundamentally important principles; and Kuhn, starting from purely theoretical reasoning, has explained rubberlike elasticity on a basis of molecular kinetics.

In renewing the study of the freezing of liquids, an idea was developed which proved to be very helpful in guiding further research, and represented a step toward a better understanding of earlier theories. This new point of view will be discussed in the following pages.

PHENOMENA OBSERVED IN THE FREEZING OF LIQUIDS

STRONG INCREASE IN THE RELAXATION TIME AS A CAUSE

Tammann[2] studied the true character of the transformation points of silicate glasses and various high-polymeric organic substances, such as polystyrene and polyindene, which Jenckel[3] and others regarded as not real, but as depending on freezing phenomena. Since a new point of view is of great advantage in making progress, the problem of freezing is approached from the point of view of the state of liquids.

It has been the general impression that the orientation of the molecules of a liquid is one of complete disorder, but the most recent researches[4] indicate that even the molecules of a liquid have a certain orderly arrangement, *i.e.*, their orientation is governed by their form and by the distribution of forces. In other words, a liquid possesses a definite structure. This structure has a relaxation period, *i.e.*, when a definite structure which at the time is in equilibrium is destroyed, *e.g.*, by a change in temperature, there is a considerable interval of time before the new structure which is formed comes to thermodynamic equilibrium. Above the melting point of the substance, this relaxation time is very short, *viz.*, about 10^{-12} to 10^{-10} second, but below the melting point, it reaches high values (provided crystallization is avoided); in fact even weeks or months may be required for equilibrium to be attained. If the time necessary for a change in state reaches the relaxation time of a process, and then begins to

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kunststoffe*, Vol. 30, No. 6, pages 170-172, June 1940.

exceed this time, it means that the process can no longer keep pace with the change in state and appears to come to a standstill. The process becomes "frozen". In the range where the times of relaxation of the structure are long, the molecules of the liquid become frozen into a well defined structure, because all changes in state take place in an interval of time which far exceeds the relaxation time of the structure. Outwardly this range is characterized by transformation of the "liquid" substance, with its molecules in motion with respect to one another, into a solid, disordered, *i.e.*, amorphous or glasslike substance, in which the molecules are oriented and spaced in rigid formation. The range within which the increase in the relaxation of the structure is rapid becomes the freezing range of the liquid[5].

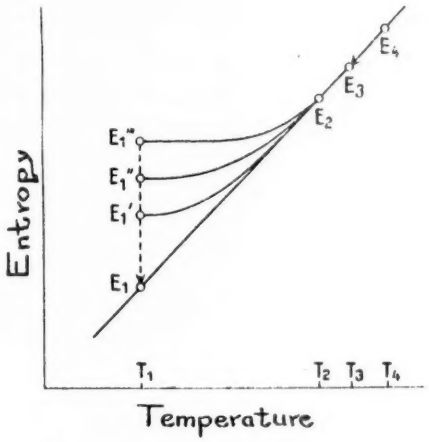

FIG. 1.—Values of the entropy in freezing range.

DIFFERENT ORDERED STATES

In developing this concept further, the occurrence of secondary effects which accompany the freezing phenomena, can be represented diagrammatically, as in Figure 1. This diagram illustrates the change in order of a liquid with change in temperature. Above the freezing range the structure reaches equilibrium immediately, *e.g.*, with a drop in temperature from T_4 to T_3 equilibrium is reached within the fraction of a second E_4 to E_3. On the contrary, below temperature T_2, at which the freezing range begins and the time of cooling is greater than the time for structural relaxation, cooling of the liquid from T_2 to T_1 freezes it in the unstable states E_1''', E_1'' and E_1' which depend thermodynamically on the time of cooling. Here secondary effects enter into play.

After a sufficiently long rest period at temperatures close to the freezing range, equilibrium E_1 is gradually reached in this way (in this case there is a secondary effect, *viz.*, the acceleration resulting from tempering at temperatures just above the freezing range, provided rapid cooling is avoided). On the other hand, at lower temperatures the time of relaxation is so great that structural equilibrium is no longer attained in a finite time. The absolute zero-point entropy[6] has therefore a finite value, which can be explained in this way[7].

VOLUME-TEMPERATURE CURVES

It is well at this time to describe in a brief way the relations between the phenomena which have just been discussed and changes in volume. The volume depends, not only on the position and orientation of the molecules, but also on the amplitude of vibration of the heat motion around this mean position. In the case of solid substances, whether crystalline or amorphous, the volume depends only on the amplitude of vibration, and even above the freezing range of the liquid, the amplitude of vibration of the heat motion outweighs the influence of the position and orientation of the molecules.

To the stable arrangement of the molecules which exists at relatively high temperatures, *i.e.*, above the freezing range, is to be attributed the greater part of the potential energy and entropy, which correspond to a higher degree of disorder. Consequently they correspond also to a greater volume than the stable ordered positions and orientations of the molecules at lower temperatures. Above

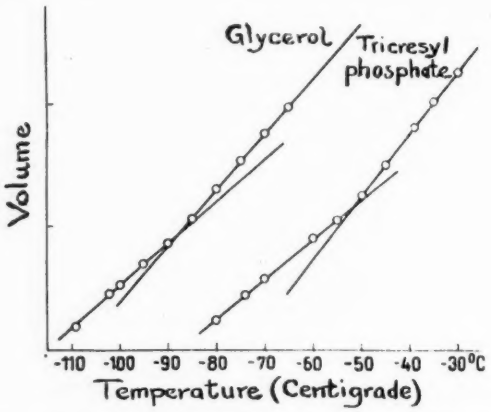

FIG. 2.—Volume curves of frozen glycerol and tricresyl phosphate.

the freezing range, the coefficient of expansion of a liquid is, therefore, greater than it is below the freezing range; and there is a change in direction of the volume-temperature curve, which indicates that the freezing range is reached. Figure 2 shows two curves of well-known liquids. The intersection of the two lines may be regarded as the temperature of the freezing range, although this is of no particular significance, since freezing takes place over a wide range.

NORMAL LIQUIDS AND LIQUIDS WITH "FIXED STRUCTURES"

LINEAR MOLECULES

Not only in the case of normal liquids, such, for example, as glycerol and tricresyl phosphate (shown in Figure 5), but also in the case of macromolecular substances, the volume-temperature curves change direction as a result of freezing. A few representative cases are shown in Figure 3 to illustrate this effect.

That a schematic representation in the same way as for normal liquids does not explain satisfactorily the peculiar characteristics of macromolecular substances is proved by experiments on the influence of chain length on the freezing temperature. If an increase in size of the macromolecules and the resulting

greater interference with one another were the only characteristics which distinguish a macromolecular substance, then the freezing temperature should increase progressively in proportion to the increase in the length of chain. However, quite the opposite is true, for the freezing temperature remains constant after initial rapid increase, as can be seen in Figure 4.

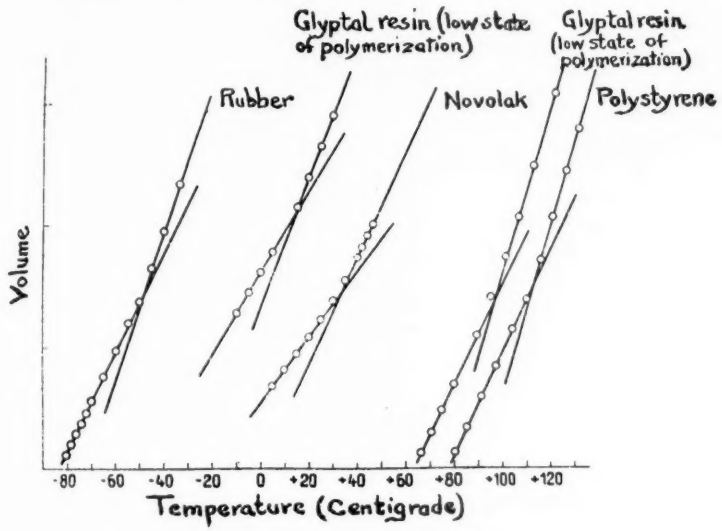

FIG. 3.—Volume curves of some macromolecular substances.

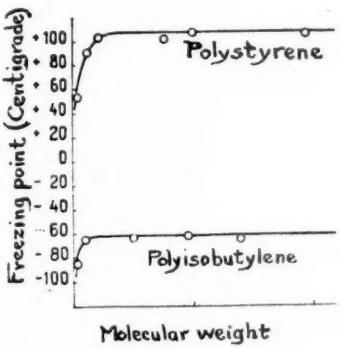

FIG. 4.—Rapid increase and subsequent constancy of the freezing temperature with increasing chain length of macromolecules.

In the following discussion, a theory is advanced whereby macromolecular substances are regarded as liquids with fixed structures, their characteristic properties are explained, and they are distinguished from frozen, low-molecular liquids.

To help in understanding the concept, a diagram is included. Figure 5 shows diagrammatically, at some particular instant, a liquid with polymerizable and condensable molecules (the individual units), which are still in monomeric form

in the liquid. This is a case of a "normal" liquid and, because of the high mobility of the individual units, its freezing temperature is very low. When these monomeric molecules polymerize or condense to a low state, as shown in Figure 6, and the individual units (chain members) have become united to one another, they lose a certain amount of their mobility, and only the terminal members retain any freedom of motion. The freezing temperature increases considerably, because the individual units which correspond to the increased time of relaxation and which have become less mobile, begin to become rigid at higher temperatures. When the degree of polymerization or of condensation becomes great enough, as illustrated in Figure 7, the freezing temperature range becomes constant, and then depends only on the mobility of the chain members with respect to one another, for the number of the remaining mobile terminal members is infinitesimally small compared to the great number of "fixed" chain members in the macromolecules. By linking of the individual units together, the resultant macrostructure has all the properties which distinguish macromolecular substances from other substances. To this extent there is good agreement with the views of Kuhn[8] and of Staudinger[9].

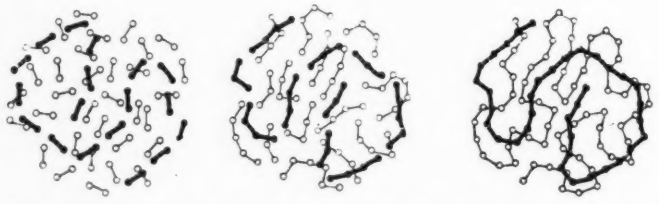

FIG. 5.—Normal liquid. Individual particles with freedom of motion with respect to one another. (Left.)
FIG. 6.—Low state of polymerization. Reduced mobility of the chain members. (Center.)
FIG. 7.—Liquid with "fixed" structure. The mobility of the chain members influences the freezing range. (Right.)

As is evident in the case of rubber, itself, which is included in the curves of Figure 3, this substance is representative of a type of macromolecular substances whose chain members are extraordinarily mobile. As a result, the freezing-point range is very low, *i.e.*, between $-60°$ C and $-70°$ C. On the contrary, tricresyl phosphate, which is an ordinary light, mobile liquid at room temperature, freezes at only $-52°$ C. In spite, therefore, of their being linked to one another, the chain members of rubberlike substances possess the highest degree of mobility with respect to one another and, by union with one another, macromolecules are formed which "fix" the chain members in such a way that macromolecular substances have stable structures even far above their freezing points. This structural stability is lost only at temperatures at which a change in position of the felted macromolecules becomes possible. In many cases this is possible only toward decomposition temperature. This corresponds to the macro-Brownian movement of Kuhn[8].

MACROMOLECULES WITH A NETWORK STRUCTURE

The formation of a network structure of macromolecules, which is so important in controlling the quality of an artificial substance, not only has an effect on the mobility of the chain members in the way already described, but offers an experimentally demonstrable proof of the theory which has been proposed. If the individual chain members link themselves together to an increasing extent

by the formation of bridges, which means the formation of a network of macromolecules, this further obstacle to the mobility of the chain members would, if the theory is correct, result in an increase in the freezing temperature.

A study of this problem was undertaken with the classic and well-known example used by Staudinger, *viz.*, the mixed polymer, styrene-*p*-divinylbenzene[10]. Figure 8 shows the volume-temperature curves. The addition of 0.9 per cent of *p*-divinylbenzene changes polystyrene so much that it swells to only a limited extent, because its macromolecules are held together by a certain number of

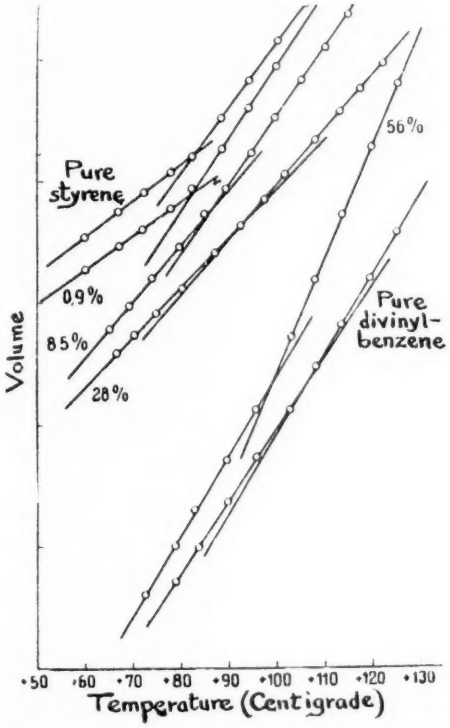

FIG. 8.—Volume curves of polystyrene with increasing percentages of *p*-divinylbenzene.

bridges. Solvents can probably penetrate into the interspaces, but can no longer bring about complete separation of the chains. However, these few cross-bonds offer little or no obstacle to movement of the chain members, and therefore the freezing temperature remains the same as that of pure polystyrene. On the other hand, an increasing number of bridges links the chain members closer and closer together, with the result that their mobility with respect to one another is greatly reduced. As a result of this, in turn, the freezing temperature increases as the system becomes more and more rigid.

In addition, the change in direction of the volume-temperature curve becomes less pronounced, because an increasing number of chain members become completely blocked in their movement through the close network, and consequently a "permanently frozen" liquid is finally formed. The few remaining mobile

chain members in this frozen liquid give evidence of their freezing by the slight break in the volume-temperature curve.

What has just been said in a more or less theoretical way applies also to technically important network reactions, which include the hardening of many resinous condensation products. Whereas Novolak contains comparatively mobile microelements in its macrostructure, as is evident in Figure 3, resinous condensation products which are thoroughly hardened have rigid macrostructures, the structural units of which are either permanently frozen or have so little mobility that they freeze only around their decomposition temperatures. Naturally this is of great importance technically, first of all because the macrostructure becomes fixed, and cold flow is prevented and, secondly, because, with the disappearance

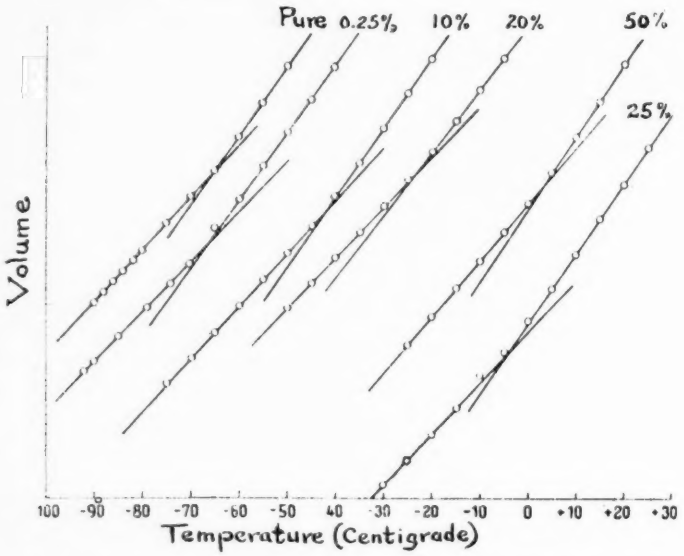

FIG. 9.—Volume curves of vulcanized rubber with increasing percentages of sulfur.

of all freezing phenomena, all sudden changes in properties and all secondary phenomena also disappear[11].

Another well known case of a reaction which involves the formation of a network, and which is at the same time of tremendous importance, is the vulcanization of rubber. A study of the volume curves of samples of rubber of increasing degrees of vulcanization, as shown in Figure 9, furnishes new proof of the correctness of the new idea that the freezing temperature increases because of a progressively diminishing mobility of the microelements of the macrostructure resulting from the formation of bridges.

IMPORTANCE OF VOLUME MEASUREMENTS OF ARTIFICIAL SUBSTANCES

The reason that volume measurements are of value lies in the fact that, after the macrostructure has increased to a certain degree, the freezing point no longer increases, but reaches a constant value which is characteristic of the particular substance. The freezing temperature is in turn closely related to the

mobility of the microelements of the macrostructure, and therefore the freezing temperature can be regarded as an index of this mobility.

There are other possible methods of explaining why different macromolecular systems differ in mobility. One possible cause is the strong influence of polar substituents; for example, the carboxyl group in polyacrylic acid and the phenyl group in polystyrene make rigid systems out of macromolecules such as those of polybutadiene, which are composed of simple CH_2 groups and are in themselves highly mobile. These rigid systems, like the other substances already mentioned, freeze at relatively high temperatures (see Figure 3).

A further point to be considered is the problem of socalled internal and external softening. However, this will be reserved for discussion in detail at another time[12]. By internal and external softening is meant the distinction between an increase in mobility of a rigid macromolecular structure by introduction of light, mobile structural units, and an increase in mobility which results from a loosening of the structure by penetration of small molecules, such as those of a solvent.

The ideas regarding macromolecular substances in the solid state, which are discussed in the present paper and which are based on purely intuitive reasoning, can be in the same way by a more theoretical line of reasoning. The concept of a liquid with a fixed structure also follows when the difference between the thermodynamic function of the state of normal liquids and of high polymers[12] is considered.

ACKNOWLEDGMENT

The author wishes to show his appreciation of the assistance of Professor Thiessen in this work.

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THE FIBROUS PROPERTIES AND ABRASION RESISTANCE OF SYNTHETIC RUBBER COMPOUNDS *

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The ability of a rubber article to resist tearing is an important factor in governing its utility. This is especially true when the article undergoes various deformations by the action of tearing forces. The fact that products made of synthetic rubber have proved excellent in practical use despite their relatively low tensile strengths can, in our opinion, be explained by the high tear resistance exhibited by synthetic rubber compounds. It is, therefore, of importance to include tear resistance tests when evaluating the properties of synthetic rubber compounds.

Two investigations—that of Busse[1] and that of Clark[2]—stand out in the comparatively small literature devoted to the fibrous properties of rubber (tear resistance).

Busse investigated the phenomena observed in the tearing of rubber, and attempted their scientific explanation. He analyzed the theory of the tearing of ideal, highly elastic media, and compared the conclusions with the behavior of rubber on tearing. On the basis of his experiments and on data collected from literature, Busse concludes that rubber compounds may exhibit two types of structure: (1) a semi-racked structure and (2) a mechanical, fibrous structure.

A semi-racked structure is characteristic of compounds which have high rubber contents and which exhibit high resistances to tearing forces. According to Busse, the development of such a structure can be explained by the existence of crystallites in the rubber, which are responsible for the Joule effect and for the diffraction patterns of x-ray diagrams. The addition of pigments tends to destroy this semi-racked structure, and concurrently to decrease tear resistance.

A mechanical fibrous structure is exhibited by compounds containing high proportions of carbon black. This type of structure is characterized by knotty, zigzag tearing, and by high tear resistance.

Busse investigated the influence of the depth of the initial cut on the value of the force necessary to start tearing in samples of different widths. He proved that the average tearing force decreases rapidly as the cut is made deeper until the cut approaches the middle of the test-piece. At this point, the force passes through a minimum, and increases rapidly when only a small portion of the width remains uncut. Busse also determined the depth of cut necessary to produce tearing of rubber strips previously stretched to a certain degree. In this way he found a relation between the depth of cut and the elongation necessary for tearing after different times of vulcanization. He further investigated the effect of temperature on the tearing of stretched rubber.

Clark's work deals with a series of problems connected with cutting and tearing tests. He found that cutting is related to the hardness and the coefficient of friction, and that tearing is a function of hardness and tensile strength.

* Translated and edited by J. Talalay for Rubber Chemistry and Technology from *Caoutchouc and Rubber* (U.S.S.R.), pages 37-48, June, 1937.

EXPERIMENTAL PART

Investigations dealing with the fibrous structure of rubber have so far dealt only with natural rubber. As yet, no data have been compiled for the synthetic sodium-butadiene polymer, which is the basic raw material of the Russian rubber industry. Our object was, therefore, to make a comparative study of the fibrous properties of natural and synthetic rubber compounds, as exhibited by their tear resistance.

In the tear tests we used specimens of various physical and chemical properties. Further we studied the characteristics of the tearing surfaces after the samples had been torn, with the object of investigating the mechanism of tear resistance and the factors which cause tearing.

The following variables were investigated with respect to their effect on tear resistance:

1. The increase in fibrous structure by mechanical treatment.
2. The time of vulcanization.
3. The plasticity of the synthetic rubber.
4. The thickness of the vulcanized test-piece.
5. The depth of the initial cut.
6. The quantity and type of filler (carbon black and zinc oxide).

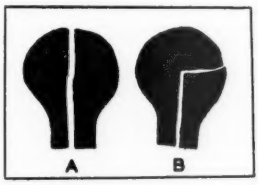

FIG. 1.

TECHNIQUE OF DETERMINING TEAR RESISTANCE

The instrument was a dynamometer commonly used for determining the tensile strengths of cotton threads. The test-pieces were circular, with a short rectangular extension (Figure 1). An incision was made along the middle of the extended section to the center of the circular part. The diameter of the circle was 48 mm. The legs of the extended section were clamped in the dynamometer, and could be stretched by means of a screw attached to the lower clamp. The speed of separation of the dynamometer clamps was 160 mm. per minute. The tearing force was recorded every 10 seconds.

The shape of the test-piece has the advantage that it allows observation of tearing in any direction almost within the 360° of a complete circle.

The tensile strength, the elongation at break, and the permanent set were determined on an Avery dynamometer. Abrasion tests were made by a Grasselli type of testing machine.

The formulas of the compounds are tabulated in Table I. The compounds were mixed on a laboratory mill.

Comparison of Synthetic and Natural Rubber Compounds Loaded with Carbon Black and Zinc Oxide

Compounds Nos. 1 to 12 (Table I) were designed for the purpose of studying the effects of varying amounts of carbon black and zinc oxide on the tear resistance and fibrous properties of the vulcanized products. These compounds are all based on Formula 2, which exhibits a pronounced irregular structural tearing. Parallel compounds of synthetic and natural rubber of otherwise identical compositions were used to permit a strict comparison of the results. Figure 2 shows the relation between the tearing force and time elapsed from the moment tearing begins. The curves are plotted for natural rubber compounds Nos. 5 and 7, and for synthetic rubber compounds Nos. 6 and 8. The corresponding data on the tensile strengths of compounds Nos. 7 and 8 are recorded in Figure 2.

Table I

Compounding Formulas

Compound No.	Synthetic rubber plasticity				Smoked sheet	Gas black Mycop	Lamp black G. E. T.	Gas black Baku	Sulfur	Accelerator	Antioxidant	Softener No. 1	Softener No. 2	Zinc oxide	Litharge	Softener No. 3
	0.31	0.40	0.53	0.87												
1	—	100	—	—	—	20	20	—	3.5	0.8	1.0	1.5	3.0	14.0	1.0	—
2	—	—	—	—	100	20	20	—	3.5	0.8	1.0	1.5	3.0	14.0	1.0	—
3	—	—	—	—	100	20	20	—	3.5	0.8	1.0	1.5	3.0	3.0	1.0	—
4	—	100	—	—	—	20	20	—	3.5	0.8	1.0	1.5	3.0	3.0	1.0	—
5	—	—	—	—	100	10	10	—	3.5	0.8	1.0	1.5	3.0	14.0	1.0	—
6	—	100	—	—	—	10	10	—	3.5	0.8	1.0	1.5	3.0	14.0	1.0	—
7	—	—	—	—	100	40	40	—	3.5	0.8	1.0	1.5	3.0	14.0	1.0	—
8	—	100	—	—	—	40	40	—	3.5	0.8	1.0	1.5	3.0	14.0	1.0	—
9	—	—	—	—	100	20	20	—	3.5	0.8	1.0	1.5	3.0	8.0	1.0	—
10	—	100	—	—	—	20	20	—	3.5	0.8	1.0	1.5	3.0	8.0	1.0	—
11	—	—	—	—	100	20	20	—	3.5	0.8	1.0	1.5	3.0	24.0	1.0	—
12	—	100	—	—	—	20	20	—	3.5	0.8	1.0	1.5	3.0	24.0	1.0	—
13	—	100	—	—	—	—	—	25	4.0	1.0	—	—	3.0	4.0	—	5.0
14	—	100	—	—	—	—	—	50	4.0	1.0	—	—	3.0	4.0	—	5.0
15	—	100	—	—	—	—	—	75	4.0	1.0	—	—	3.0	4.0	—	5.0
16	—	100	—	—	—	—	—	100	4.0	1.0	—	—	3.0	4.0	—	5.0
17	110	—	—	—	—	—	—	50	3.0	1.0	—	—	3.0	4.0	—	—
18	—	100	—	—	—	—	—	50	3.0	1.0	—	—	3.0	4.0	—	—
19	—	—	100	—	—	—	—	50	3.0	1.0	—	—	3.0	4.0	—	—
20	—	—	—	100	—	—	—	50	3.0	1.0	—	—	3.0	4.0	—	—
21	—	100	—	—	—	—	—	25	4.0	1.0	—	—	3.0	4.0	—	—

A comparison of the results obtained with synthetic and natural rubber compounds of this series makes possible the following conclusions. An increase in the active carbon black content from 10 to 40 per cent results in a much higher tear resistance for both synthetic and natural rubber compounds.

Mixtures containing 3, 8, 14 and 24 parts of zinc oxide show that the highest tear resistances, tensile strengths and elongations are obtained by using 8 to 14 parts of zinc oxide (natural rubber compounds Nos. 3, 9, 2 and 11). Similar synthetic rubber compounds (compounds Nos. 4, 10, 1 and 12) show improvements in tear resistance by the addition of zinc oxide, whereas the latter has little effect on tensile strength and elongation.

It is important to note that, in nearly all cases, short times of vulcanization give the better tear resistance values. After short cures, tearing does not begin until the sample has undergone considerable elongation. Overcured samples tear almost immediately at comparatively small loads.

Synthetic Rubber Compounds Containing Carbon Black

To study the reinforcing effect of carbon black on synthetic rubber, a series of compounds containing 25, 50, 75 and 100 parts by weight of gas black were prepared (compounds Nos. 13, 14, 15 and 16). Each batch was divided into two

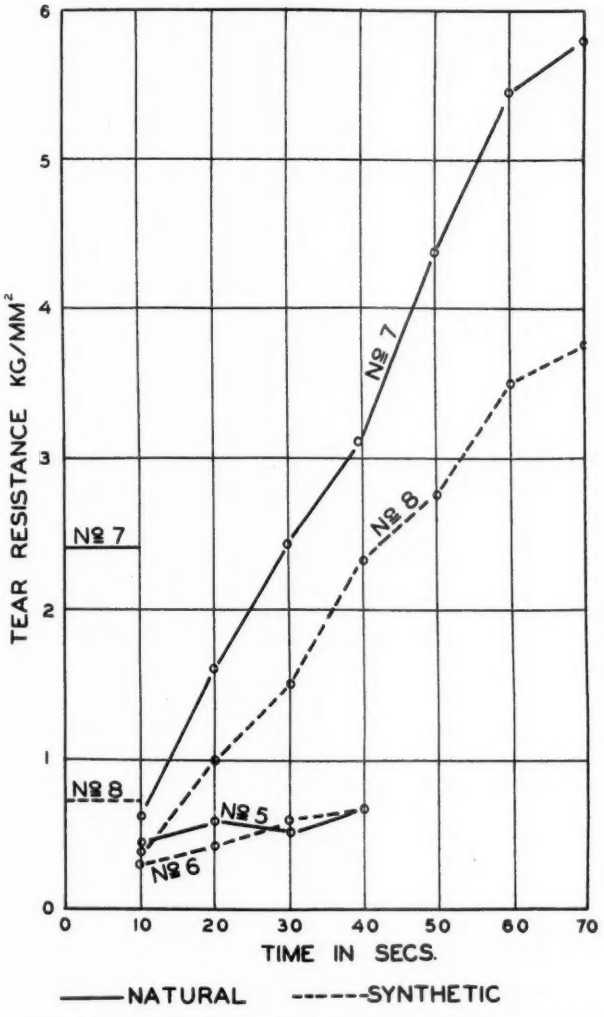

Fig. 2.—Comparison of tear resistances of natural rubber compounds Nos. 5 and 7, and synthetic rubber compounds Nos. 6 and 8. Tensile strengths of compounds Nos. 7 and 8 are indicated by short horizontal lines. All samples were vulcanized for 30 minutes.

parts. One part was passed through the calander in the usual way; the other was run through the nip of the rolls for 8 minutes to produce a more pronounced grain.

The samples were examined for tensile strength, tear resistance, elongation, permanent set, and abrasion.

The results are tabulated in Tables II, III, IV and V. Figure 3 shows graphi-

TABLE II

TEAR RESISTANCE OF COMPOUNDS NOS. 13-16

Compound No.	Vulcanization (minutes)	A—along B—perpendicular to direction of calandering	Tearing force in kg. per sq. mm. after time (minutes)						
			10	20	30	40	50	60	70
13	10	A	0.18	0.22	0.55	0.65	0.67	—	—
		B	0.44	0.70	0.88	1.00	1.14	1.17	1.17
13	20	A	0.45	0.72	0.77	0.81	—	—	—
		B	0.26	0.61	0.72	0.76	—	—	—
13	40	A	0.29	0.53	0.62	—	—	—	—
		B	0.21	0.49	0.58	—	—	—	—
13	60	A	0.27	0.27	—	—	—	—	—
		B	0.26	0.27	0.27	—	—	—	—
13	80	A	0.26	0.27	—	—	—	—	—
		B	0.23	0.38	0.58	—	—	—	—
14	10	A	0.45	0.75	0.92	1.13	1.37	1.54	1.71
		B	0.41	0.63	0.96	1.03	1.16	—	—
14	20	A	0.53	1.06	1.30	1.53	1.77	1.83	—
		B	0.77	1.17	1.50	1.76	1.84	1.90	—
14	40	A	0.72	1.12	1.76	2.40	—	—	—
		B	0.78	1.39	2.06	2.24	2.60	—	—
14	60	A	0.81	1.67	2.13	2.50	—	—	—
		B	0.91	1.84	2.50	2.61	—	—	—
14	80	A	0.57	1.21	1.79	1.87	—	—	—
		B	0.70	1.27	1.83	1.87	—	—	—
15	10	A	0.83	1.42	1.81	2.02	2.10	—	—
		B	0.65	1.39	1.83	2.09	2.33	2.83	—
15	20	A	1.03	1.56	2.08	2.44	2.63	2.96	3.10
		B	1.15	1.78	2.30	3.04	3.70	3.96	3.96
15	40	A	0.89	1.77	2.80	3.30	4.03	—	—
		B	1.02	2.03	2.84	3.31	3.65	3.78	—
15	60	A	0.80	1.68	2.64	3.20	3.24	—	—
		B	0.88	1.88	2.80	3.16	3.22	—	—
15	80	A	0.79	1.26	1.74	2.50	2.77	—	—
		B	0.77	1.62	2.24	2.38	2.86	—	—
16	10	A	0.95	1.62	2.00	2.25	2.40	—	—
		B	1.08	1.85	2.41	2.84	3.20	3.25	—
16	20	A	1.00	1.80	2.30	2.56	—	—	—
		B	0.98	1.94	2.30	2.64	3.04	3.08	—
16	40	A	0.89	1.30	1.41	—	—	—	—
		B	0.77	1.27	1.89	2.40	2.70	—	—
16	60	A	0.89	1.56	1.66	—	—	—	—
		B	0.96	1.42	1.69	—	—	—	—
16	80	A	1.25	1.34	—	—	—	—	—
		B	0.98	1.22	—	—	—	—	—

TABLE III

TENSILE PROPERTIES OF COMPOUNDS NOS. 13-16

Compound No.	Vulcanization (minutes)	A—along B—perpendicular to direction of calandering	Tensile strength (kg. per sq. mm.)	Elongation at break (percentage)	Permanent set (percentage)
13	10	A	0.36	885	52
		B	0.38	845	60
13	20	A	0.60	525	32
		B	0.38	540	60
13	40	A	0.35	230	8
		B	0.53	325	12
13	60	A	0.45	220	12
		B	0.51	250	12
13	80	A	0.45	230	8
		B	0.55	275	8
14	10	A	0.54	730	108
		B	0.58	800	100
14	20	A	1.00	500	60
		B	1.10	555	72
14	40	A	1.06	400	48
		B	1.10	405	60
14	60	A	1.04	315	28
		B	1.13	340	36
14	80	A	1.10	330	32
		B	0.95	270	20
15	10	A	0.84	445	76
		B	0.89	490	76
15	20	A	1.71	370	48
		B	1.15	410	46
15	40	A	1.11	255	36
		B	1.17	280	36
15	60	A	1.08	240	28
		B	1.08	225	24
15	80	A	1.14	215	24
		B	1.28	235	22
16	10	A	1.77	410	72
		B	0.82	390	80
16	20	A	0.93	245	44
		B	0.91	230	44
16	40	A	1.06	160	28
		B	1.12	200	40
16	60	A	1.12	160	24
		B	1.12	175	22
16	80	A	1.23	145	24
		B	1.02	120	20

cally the tear resistances and tensile strengths of these four compounds after 10 minutes vulcanization. As above, it is obvious that loading synthetic rubber compounds with active carbon black results in a substantial increase in tear resistance.

Optimum resilience (tensile product) is obtained with 50 per cent of carbon black. The best abrasion results are obtained with compound No. 14 (50 per cent Black), and the poorest results with compound No. 16 (100 per cent Black). For example, the optimum tensile product and abrasion resistance occur together at a carbon black concentration of 50 per cent.

Taking all these factors into consideration, it appears that the best all-round physical properties are obtained for synthetic rubber compounds at a carbon black concentration between 50 and 75 per cent by weight, and more probably nearer 75 per cent.

TABLE IV

ABRASION OF COMPOUNDS NOS. 13-16 (CC. PER H. P. PER HR.) MEASURED BY A GRASSELLI MACHINE

Compound No.	Vulcanization time (minutes)				
	10	20	40	60	80
13	583	422	487	458	584
14	543	407	379	387	467
15	509	432	459	481	531
16	511	550	573	539	592

TABLE V

ABRASION TESTS OF COMPOUNDS NOS. 14F-16F, HAVING ARTIFICIALLY INDUCED GRAIN

Compound No.	A—along B—perpendicular to calander direction	Vulcanization time (minutes)				
		10	20	40	60	80
14F	A	560	389	424	452	506
	B	400	340	322	367	355
15F	A	447	471	510	567	548
	B	407	417	382	417	409
16F	A	501	461	540	634	658
	B	687	410	420	456	654

The calander effect is clearly shown in the increased tensile values of samples cut perpendicular to the direction of sheeting (marked B in Tables II and III). Only in four cases out of twenty did samples cut in the direction of sheeting give higher tensile strengths than those cut perpendicular to the direction of calandering.

An induced fibrous structure has a distinct effect on abrasion resistance. Differences up to 35 per cent in abrasion resistance are obtained in tests where the abrasive surface moves parallel and perpendicular to the direction of the fibers. This holds true irrespective of the degree of vulcanization (Table V).

PLASTICITY OF SYNTHETIC RUBBERS AND TEAR RESISTANCE

To study the effect of the plasticity of synthetic rubber on the tear resistance and the fibrous properties after vulcanization, four compounds were prepared from synthetic rubbers having plasticities of 0.31, 0.40, 0.53 and 0.87. The compounds were passed through the calander, and were vulcanized in a press

at 3 kg. per sq. cm. steam pressure. Samples were tested for tensile strength and tear resistance. The results are presented graphically in Figure 4.

Compounds Nos. 18 and 19, of medium plasticity (0.40 and 0.53), exhibit the

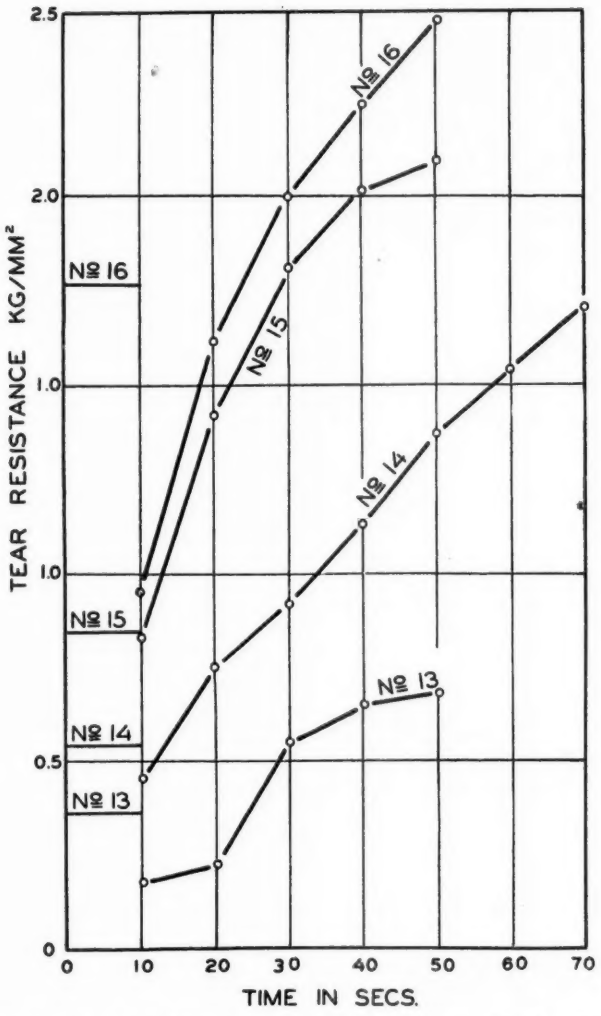

FIG. 3.—Comparison of tear resistances of four synthetic rubber compounds containing different proportions of carbon black. Tensile strengths are indicated by short horizontal lines. All compounds were vulcanized for 10 minutes.

best tear resistances and tensile products. Compound No. 20 (plasticity 0.87) has good tear resistance, but shows poor mechanical properties.

It should be mentioned here that the synthetic rubbers, apart from their different plasticities, also differ slightly in alkalinity. This additional variable affects the time of optimum vulcanization, and makes a strict comparison of the tests impossible.

Effect of Thickness of Samples on Tear Resistance

An attempt was made to learn whether it is possible to relate the dynamometer reading to the thickness of the specimen. In other words, has the thickness of the sample a strictly additive effect on the tear resistance?

Samples of compound No. 21 were prepared in four different thicknesses (approximately 0.7-0.8, 1.0-1.2, 2.2-2.4, and 3.3-3.4 mm.), and their tear resistances and tensile strengths measured. Half the samples were vulcanized for 20 minutes; the other half for 60 minutes.

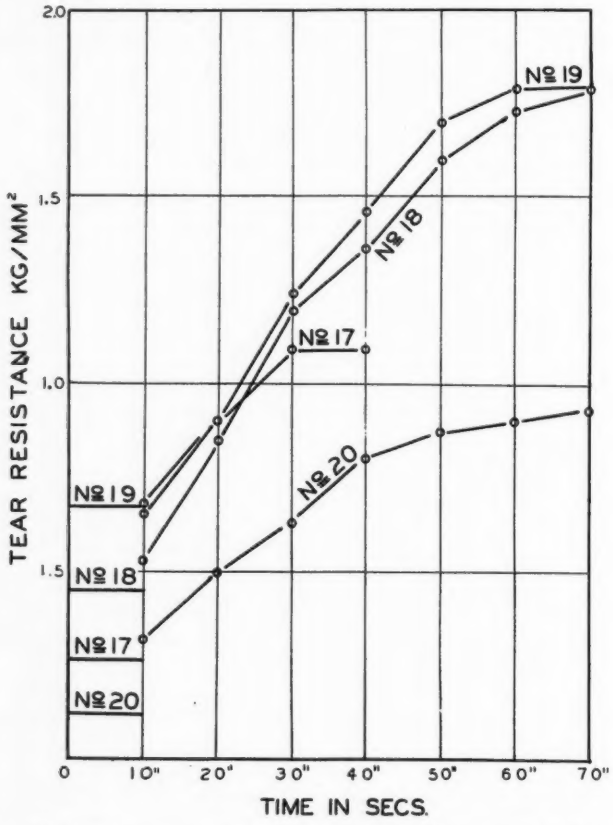

Fig. 4.—Tear resistances of compounds made from synthetic rubbers of varying plasticities. Tensile strengths are indicated by short horizontal lines. All compounds were vulcanized for 10 minutes.

It appears that the tearing loads do not increase in proportion to the thickness of the specimens. When comparing tear resistance values, it is necessary, therefore, to keep the thickness of the test samples within close limits.

The tensile strength is not affected by variations in thickness.

Depth of Cut and Tear Resistance

The work of Busse[1], already referred to, contains an interesting investigation of the influence of the depth of cut on the tear resistance of the remaining uncut portion of a rubber specimen.

Experiments similar to those of Busse were made for the purpose of comparing synthetic and natural rubbers. Compounds Nos. 11 and 12 were used. The samples were vulcanized for 10, 30 and 60 minutes.

TABLE VI

INFLUENCE OF DEPTH OF CUT ON TEAR RESISTANCE

Sample width 13 mm.					Sample width 20 mm.				
Compound No.	Vulcanization (minutes)	Depth of cut (mm.)	Width of uncut part	Tear resistance (kg. per sq. mm.)	Compound No.	Vulcanization (minutes)	Depth of cut (mm.)	Width of uncut part	Tear resistance (kg. per sq. mm.)
11	10	0	13	1.38	11	10	0	20	1.62
		1	12	0.40			2	18	0.62
		5	8	0.36			5	15	0.23
		8	5	0.18			10	10	0.38
		11	2	0.38			15	5	0.47
		12	1	1.30			18	2	0.94
11	30	0	13	1.55	11	30	0	20	1.61
		1	12	0.45			2	18	0.32
		5	8	0.26			5	15	0.37
		8	5	0.49			10	10	0.31
		11	2	0.43			15	5	0.32
		12	1	0.80			18	2	0.43
11	60	0	13	1.56	11	60	0	20	1.39
		1	12	0.23			2	18	0.23
		5	8	0.14			5	15	0.18
		8	5	0.26			10	10	0.42
		11	2	0.28			15	5	0.44
		12	1	0.47			18	2	0.48
12	10	0	13	0.51	12	10	0	20	0.49
		1	12	0.20			2	18	0.18
		5	8	0.17			5	15	0.19
		8	5	0.19			10	10	0.23
		11	2	0.42			15	5	0.40
		12	1	0.50			18	2	0.38
12	30	0	13	0.43	12	30	0	20	0.44
		1	12	0.22			2	18	0.17
		5	8	0.22			5	15	0.16
		8	5	0.21			10	10	0.12
		11	2	0.25			15	5	0.15
		12	1	0.25			18	2	0.25
12	60	0	13	0.44	12	60	0	20	0.37
		1	12	0.20			2	18	0.11
		5	8	0.14			5	15	0.11
		8	5	0.13			10	10	0.13
		11	2	0.22			15	5	0.19
		12	1	0.30			18	2	0.32

Two sizes of rectangular samples were cut from the vulcanized sheets. Both were 8 cm. long; one size was 1.3 cm. wide, the other 2.0 cm. wide. Incisions of various depths were made perpendicular to the long edge of the specimen. The samples were torn on an Avery dynamometer, and the forces necessary for tearing were noted. The results are given in Table VI, and comparative

values for natural and synthetic rubbers, vulcanized 10 minutes, are plotted in Figure 5.

These results confirm the previously expressed opinion that, under certain conditions, synthetic rubber has good tearing properties. Although an incision in a specimen of natural rubber, 1/10-1/13 of the sample width, reduces the tear resistance of the remaining portion 3-6 times, this decrease is only 2-2.5 times in the case of synthetic rubber. Further, the tear resistance of the remaining part does not change much in synthetic rubber with increasing time of vulcanization. In natural rubber, however, this value falls off very rapidly with increase in the state of cure.

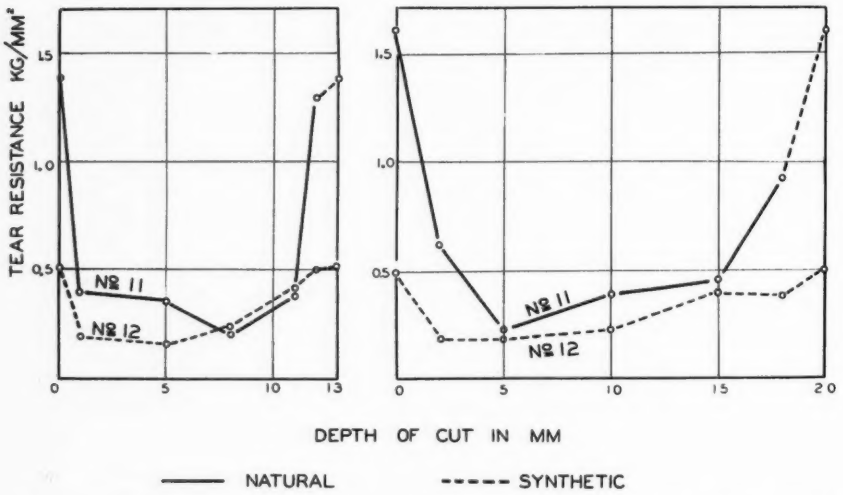

FIG. 5.—Graphs of tear resistance as a function of the depth of cut. Natural rubber compound No. 11 and synthetic rubber compound No. 12 were used. The two parts of the diagram show results for test-pieces of two different widths.

STRUCTURAL FORM OF TEARING OF SYNTHETIC RUBBER COMPOUNDS

Apart from the experimental data given above, the character and peculiarities of the torn surfaces were examined visually. Examples of some of the tears are shown in Figures 6 and 7. Both synthetic and natural rubber compounds show different types of structural tearing, such as knotting, zigzag, concentric-segment formation, and so forth[3]. These phenomena are observed only in compounds containing not less than 20 per cent of carbon black, in the presence of zinc oxide. The latter ingredient plays an important part in the development of the characteristics of the tear. Structural tearing appears at about 8 per cent of zinc oxide in the compound.

The effect of calander grain is shown clearly by some of the samples. Compound No. 7, for example, exhibits tearing of type A for a cut parallel to the grain, and type B for a cut perpendicular to it (Figure 1). A similar effect is observed for samples made from compound No. 21, cured for 60 minutes. It is remarkable, however, that attempts to increase artificially the orientation of the fibrous structure of the rubber by additional calandering, did not always produce the result expected. This is probably due to the fact that, to make a good calandered sheet, an accumulation of compound must be built up between

the rolls. This accumulated bank destroys the orientation of the particles, and the desired effect is not produced.

The state of cure is another important factor in the building up of a fibrous structure. In nearly all the experiments, samples vulcanized for 10 minutes, and some for even 20 minutes, show simple forms of tearing surfaces of the type A and B (Figure 1), or some intermediate. Specimens given their optimum times of cure of 30 and 40 minutes, and some specimens cured 60 minutes, are characterized by intricate, irregular forms of tearing. Examples of these for synthetic rubber are shown in Figures 6 and 7 (C, D and E). Types of tearing surfaces C and D (Figure 6) recur with great consistency at optimum vulcanization. In fact it is possible to judge optimum cure merely by observing the design of the tearing surfaces. After the optimum has been passed, the shape of the tear once more becomes smooth and regular.

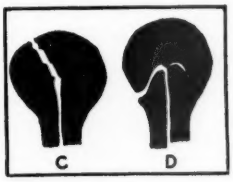

FIG. 6.

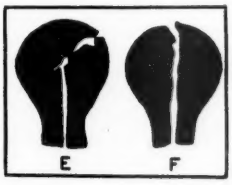

FIG. 7.

These observations should prove of great future interest from a theoretical point of view, but lack of experimental material at this stage does not yet make it possible to offer any suggestions as to the mechanism of the tearing of rubber.

SUMMARY

1. A method of measuring the tear resistance of rubber compounds was developed. This method has a number of advantages over other methods (Goodrich, Heidensohn, Goodyear, etc.), including the following. (a) The symmetrical shape and the large surface of tearing (20 sq. cm.). This excludes the possibility of short, accidental tears, and enables better observation of the nature of the tear. (b) Owing to the small size of the clamped portion of the specimen compared to the size of the tearing surface, "end effects" are largely eliminated. (c) Tearing forces are registered periodically (every 10 seconds), and it is possible in this way to determine the total energy expended on tearing, and the nature of its changes. (d) The experiments are easy to perform, and the apparatus is simple.

2. The addition of carbon black (10-100 per cent) to synthetic rubber compounds increases considerably the tear resistances of the vulcanized products.

The best results are obtained with compounds containing between 50 and 75 per cent of carbon black.

3. A zinc oxide content of between 8 and 14 per cent improves the tear resistances of compounds of both synthetic and natural rubbers.

4. Compounds with increased fibrous structure show increased abrasion resistance when the fiber direction is parallel to the movement of the abrading surface.

5. Compounds cured for short times only show low tear resistances when made of synthetic rubbers of both low (0.31) and high (0.87) plasticity. The best results are obtained with compounds made of synthetic rubber of medium plasticity (0.53 and 0.40) (see Figure 4).

6. When comparing tear resistances, it is of the utmost importance to maintain the thickness of test-specimens within narrow limits. It is desirable to keep variations within 10-15 per cent.

7. The weakening of the uncut portion of a test-specimen with increase in depth of cut is less pronounced with compounds of synthetic rubber than it is with natural rubber compounds, particularly in the case of overcured samples. With synthetic compounds, this weakening effect varies 2-3 times; with natural rubber compounds it is 3.5-6.5 times. The relation between tear resistance and depth of cut is shown in Figure 5 and Table VI.

8. Carbon black compounds of both synthetic and natural rubbers exhibit various structural forms of tearing. Synthetic rubber compounds with low tear resistances show simple and smooth tearing surfaces, usually in the prolongation of the cut, or at a slight angle to it (Figure 1, type A or intermediate between A and B). Synthetic compounds with high tear resistances show complicated tearing surfaces (Figures 6 and 7, types C, D, E and F).

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[3] J. Rubber Ind. (U.S.S.R.), No. 5, **1936**.

INTRODUCTION OF THE BENDING-STRENGTH TEST AS A MEANS OF DETERMINING THE FREEZING POINT AND CHANGES IN ELASTIC PROPERTIES OF SOFT RUBBER AT HIGH AND LOW TEMPERATURES *

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The constantly increasing demands of late for natural rubber and synthetic rubber products which are stable at low temperatures were sufficient inducement to search for a satisfactory testing method by which the behavior of these products at low temperatures could be determined with reasonable accuracy.

The cold closets to be found in so many laboratories are not satisfactory for an investigation of this kind, because they ordinarily can be used only down to $-35°$ C, whereas the majority of rubber mixtures do not become hard at this temperature. Even cold closets which are specially designed for use at temperatures down to $-60°$ C, and which frequently are equipped with two compressors, are not satisfactory in an investigation of this kind because not all rubber mixtures become hard, even at $-60°$ C. Also the prices of cold closets of this kind are very high. Cold closets have been used for studying changes in the softness and elasticity of rubber mixtures, but for the reasons given, they have been unsuitable for determining freezing points.

In the literature may be found two low-temperature methods which are used for rubber. The first of these methods was described by Gibbons, Gerke and Tingey in 1933, as development work of the United States Rubber Company, under the title of "The T-50 Test for State of Vulcanization" (cf. *Ind. Eng. Chem. Anal. Ed.* **5**, 279 (1933); Rubber Chem. Tech. **6**, 525 (1933)). In this test, a dumb-bell strip is frozen while stretched, is then warmed slowly, and the temperature at which the sample has contracted to 50 per cent of the maximum extension is determined. According to investigations of the authors, this temperature is a function of the degree of vulcanization, as judged, for example, by the free or combined sulfur. The method is therefore adapted primarily to the determination of the state of vulcanization. On the other hand, it is not suitable for the determination of the freezing point of a rubber mixture or for the determination of changes in its physical properties at low temperatures, because it gives no information which can be used in calculating the modulus of elasticity or the spring constant. Nor is it possible by this method to determine the freezing point of a rubber mixture.

The second method for studying the behavior of soft rubber at low temperatures was first described in a paper of the Research Laboratory of the I. G., Ludwigshafen, under the title "Kälteprüfgerät für Kunststoffe" in 1938 (cf. *Kunststoffe* **28**, No. 7 (1938)). In this method a test-specimen, $15 \times 60 \times 0.5$ mm., is bent over in the middle, and is clamped under a spring which is fastened on

* Translated for Rubber Chemistry and Technology from *Kautschuk*, Vol. 16, No. 12, pages 151-156, December 1940.

a block, over which is a falling weight. The whole apparatus is installed in a cooling chamber, which can be maintained at the desired temperature by a current of air blown through carbon dioxide ice. The weight is made to fall on the looped part of the test-specimen at different low temperatures, and the temperature at which the specimen breaks is observed. This method is unsuitable for determining the changes in physical properties of a product for the same reasons that the T-50 test is unsuitable.

Various other testing machines have at times been used for testing the stability of materials at low temperatures. In the first place machines have been designed for pressure tests. For example, rubber cylinders with diameter equal to the height, or else cubes, are enclosed in a double-walled container, through which a pressure rod extends. The jacket is surrounded with a cooling liquid.

This kind of test has the disadvantage that the procedure is tedious and time-consuming, involves complicated apparatus, and shows high thermal losses, and the apparatus has a strong tendency to form ice. A further disadvantage of experiments of this kind is that temperatures below $-70°$ C cannot as a rule be attained.

In the problem concerned in the present investigation, it was necessary to find a new technique, with special attention to the following points:

(1) The freezing point must be determined by some reliable method.

(2) The temperature must be reached quickly and maintained at any point between 0° C and $-78°$ C for the desired length of time.

(3) The testing apparatus must have only a small heat capacity so that significant thermal losses are avoided, and it must operate satisfactorily at low temperatures.

(4) It must be possible to insert the test-specimen quickly in the apparatus, and to change to a new specimen quickly so that thermal losses are avoided.

(5) In addition to determining the freezing point of a test-specimen, it must be possible to determine reliably and accurately the changes which take place in the elastic properties of the test-specimen, especially its modulus of elasticity.

These five requirements are not fulfilled by any of the testing methods now in general use for soft rubber, such as tensile strength, resistance to compression, torsion resistance, elasticity and hardness. Attention was, therefore, directed first of all to adapting the bending test to the particular requirements. Preliminary experiments at room temperature gave such promising results that an apparatus was constructed by which it was possible to carry out measurements at both high and at the lowest temperatures desired.

THE EXPERIMENTAL APPARATUS

For tests at room temperature and at elevated temperatures, the apparatus shown diagrammatically in Figure 1 was employed. In this diagram, a is the test-specimen, the measurement of which will be described later. This test-specimen rests on rails, 2 cm. apart, under the upright support b. This upright support is made of thin sheet aluminum. The pressure rod c is made of hard rubber, and its weight, including that of the disc for carrying the weight d, is 15 grams. The deflection of the test-specimen as a result of the weight applied is read to one-hundredth of a millimeter on the micrometer clock gauge 3. Thousandths of a millimeter can be estimated.

From the load applied and the resulting deflection, the bending modulus E can be calculated by the formula:

$$E = \frac{PI^3}{48\,fl}$$

where P is the load in kilograms, l the span between the supports, f the deflection in cm., I the moment of inertia ($bh^3/12$), b the width of the specimen in cm., and h the height of the specimen in cm.

The apparatus is so adjusted and test-specimens are so chosen that only very small loads are necessary, *viz.*, of the order of magnitude of 100 to 150 grams. These loads are so chosen that the deflections are between 0.75 and 1.25 mm. The moduli of elasticity corresponding to these deflections are in good agreement with the moduli of elasticity obtained under pressure.

For measurements at low temperatures, the apparatus described above is removed from its bedplate, and is fastened to a hemispherical foot made of

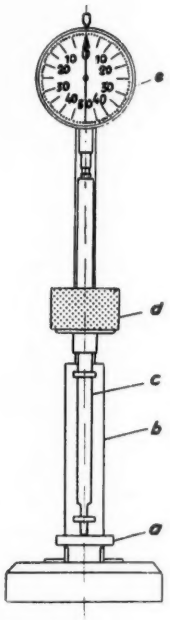

FIG. 1.—Apparatus for determining changes in the elastic properties of soft rubber.

hardwood. This assembly is then inserted in a glass tube of 30 mm. internal diameter (see Figure 2). In this form of apparatus, the pressure rod is lengthened, and is passed through a cork stopper at the upper end of the glass tube. A thermoelement is installed in the immediate proximity of the rod shaped test-specimen. This thermoelement is calibrated so that the temperature can be read on the millivoltmeter to an accuracy of 0.1° C.

The glass tube with the deflection testing appliance installed is placed in a Dewar vessel, which contains a mixture of carbon dioxide ice and acetone for maintaining a temperature of −78° C. The Dewar vessel is held in place out of contact with the glass tube by a conical stopper at the top.. The micrometer tube is held in the Dewar vessel by means of a suitable contrivance so that it can be adjusted vertically.

In position A, shown in Figure 2, the apparatus is in correct position for freezing the test-specimen. At the beginning of the freezing operation, no load is placed on the disc carrier, and the pressure rod alone rests with its own weight

of 15 grams (the same weight as that of the pressure rod used for measurements at room temperature) on the test-specimen. Freezing of a test-specimen, which involves cooling of the apparatus from room temperature to −70° C, requires about twelve minutes.

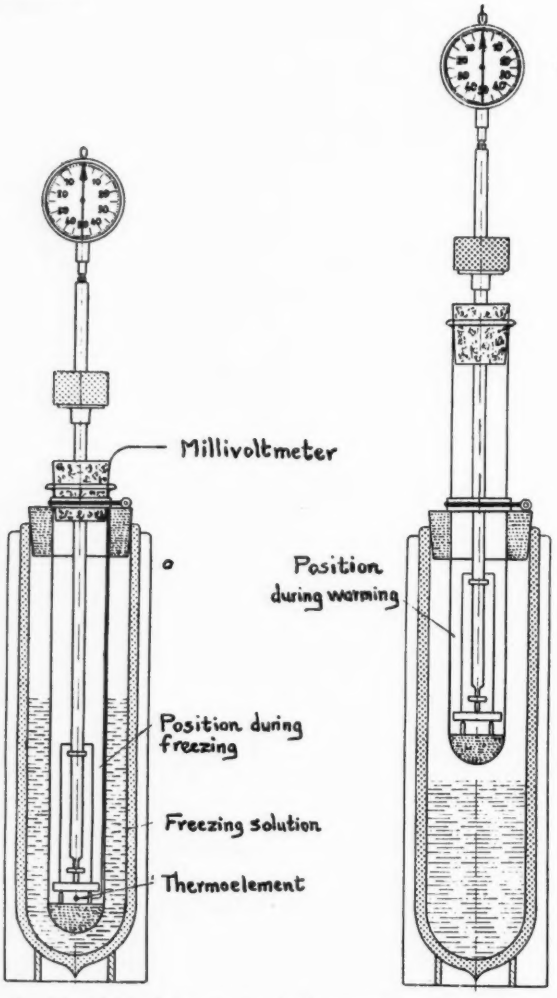

FIG. 2.—Apparatus for determining changes in the elastic properties of soft rubber at low temperatures, and for determining freezing.

To determine the freezing point, the plunger tube is withdrawn from the freezing solution to a definite height after the test-specimen has been frozen, and is fastened by a clamping device (see Figure 2, diagram B). The exact height to which the tube is raised will be discussed later.

As the temperature of the test-specimen slowly increases, the freezing point is finally reached, and the specimen begins to show a deflection, which is indicated on the micrometer. The temperature is then read by means of the millivoltmeter.

TEST-SPECIMENS

Prismatic bars, 6 mm. wide, 28 mm. long and 2-6 mm. high (depending on the stiffness) were used as test-specimens. The height was varied to this extent so that even the hardest samples could be measured with as nearly the same loads as possible. In measuring the height of a test-specimen, the degree of softness was first of all measured by specification DVM-3503 of the Deutsche Industrienormen. With the softness number obtained by this method, the height of the test-specimen was determined from the curve shown in Figure 3.

This curve was a resultant of a large number of tests, in which test-specimens of various heights were used, so that a deflection of approximately 1 mm. was obtained in all cases with the same loads. In operating thus, it is important to have the height of the test-specimen correct to avoid overloading the apparatus, and to operate under conditions as nearly constant as possible.

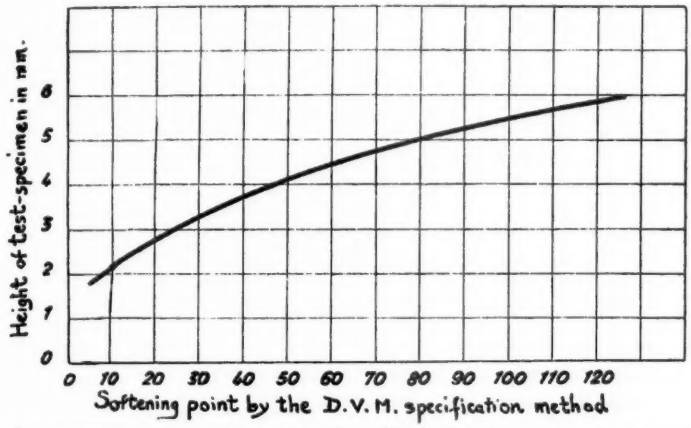

FIG. 3.—Curve for the determination of the height of test-specimens of rubber of different degrees of hardness.

EXPERIMENTAL PROCEDURE FOR DETERMINING THE FREEZING POINT

With test-specimens prepared in the way just described, the first step was to determine the load which, at room temperature, caused a deflection of 0.9-1.1 mm. The weight of the pressure rod was regarded as a preliminary weight, and therefore was disregarded. The load and the deflection were recorded after 3 hours, and the modulus of elasticity was calculated from these values. The test-specimen was then placed in the apparatus within the glass tube, and the assembly was placed in the freezing solution in the Dewar vessel. In this operation the pressure rod was left unloaded. The drop in temperature was followed by the millivoltmeter. As a rule, a temperature of about $-75°$ C was reached after 12 minutes. At the end of this time the test-specimen was completely frozen, a change which was recognizable at once by the metallic sound made by the pressure rod when it was allowed to fall on the test-specimen, and was further recognizable by the fact that, when the micrometer tube was set on the pressure rod and weights were added, there was no longer any deflection except for a slight elastic springing of a few hundredths of a millimeter.

The plunger tube was then withdrawn from the freezing solution far enough so that the increase in temperature in the neighborhood of the freezing point

was approximately 1° C per minute. With this rate of warming, it seemed safe to assume that there was no temperature lag in the test-specimen. When the freezing point was known beforehand through having been determined in a preliminary experiment, the length of the tube projecting out of the Dewar vessel was determined from curve b in Figure 4. This curve was constructed from actual measurements, and by its use the prescribed rate of warming in the neighborhood of the freezing point was assured without loss of time by first having to carry out trial tests.

After the plunger tube has been adjusted, the micrometer clock-gauge is rested on the pressure rod (the pressure of the micrometer gauge, in the present case 50 grams is taken into account for all loads), the triple loading for the deflection

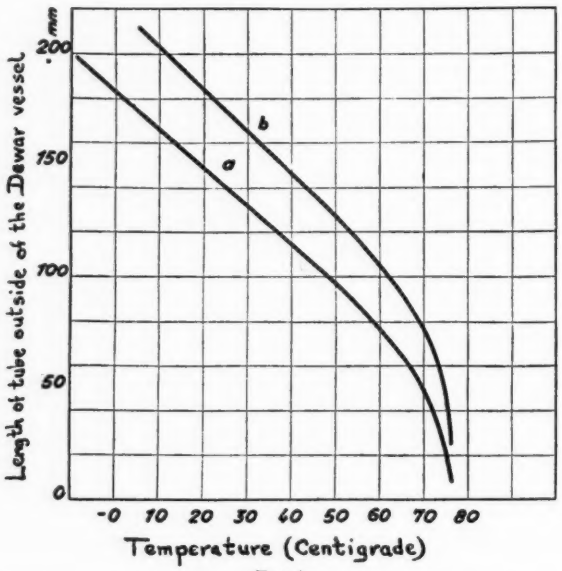

FIG. 4.
a. Curve for determining the position of the plunger tube for approximately constant temperatures for long periods of time.
b. Curve showing the position of the plunger tube with uniform heating (approximately 1° C per minute) in the neighborhood of the expected freezing point.

at room temperature is placed on the pressure rod, the micrometer clock-gauge is adjusted to zero reading, and the time, temperature and deflection are read simultaneously and are recorded. According to the height of the freezing point, the time and deflection are again read after one, two or three degrees rise in temperature.

When this procedure is followed, the first thing observed is that, instead of the expected drop in the micrometer clock-gauge hand as a result of the deflection of the test-specimen, the hand indicates an increase. This increase is attributable to expansion of the pressure rod caused by the rise in temperature. These heating curves are characteristic of the different positions of the plunger tube. The curves for the most commonly used positions of the tube are shown in Figure 5. In this case a metal rod was used as the test-specimen so that deflections at the different temperatures were certain to be avoided. With this set of curves are included curves showing the corresponding rates of heating.

The relation between the position of the plunger tube on the one hand and the rate of temperature increase on the other hand is evident from this graph. The heating curves recur in every freezing point determination, and hence must be taken into account.

In the neighborhood of the freezing point, expansion of the pressure rod apparently becomes progressively smaller, and finally changes to an apparent contraction. The cause of this lies in the initial deflection of the test-specimen. Time, temperature and deflection readings are continued until the total deflection of the test-specimen is approximately 1 mm., *i.e.*, 100 divisions on the scale of the micrometer clock-gauge. The experiment is then discontinued, and from

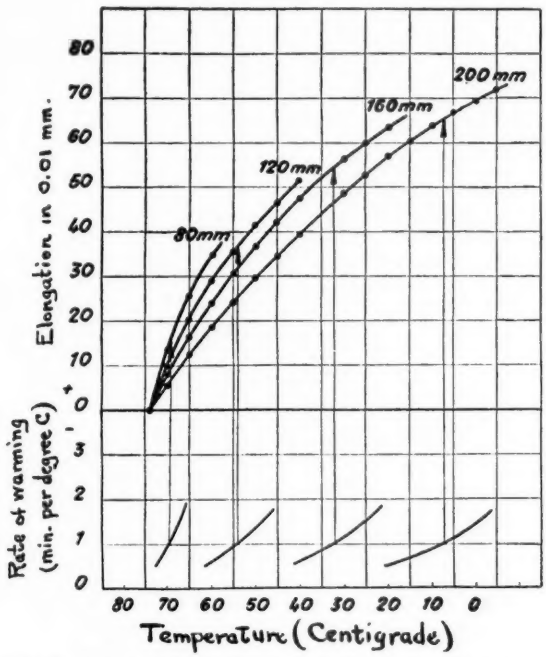

FIG. 5.—Curves of the elongation of the pressure rod for different positions of the plunger tube.

the data collected, a diagram is constructed, from which the freezing point can be determined with a precision of almost one-tenth of a degree. From data on a number of industrial mixtures, diagrams for determining freezing points were constructed. These are shown in Figure 6.

Here the abscissas represent temperatures and the ordinates expansions of the pressure rod and deflections of the test-specimen. The broken curves show the expansions of the pressure rod. The deflection curve of the test-specimen is shown in complete form. The freezing point is regarded as the point at which the deflection curve becomes tangent to the expansion curve of the pressure rod. In Figure 6 these points are indicated by arrows.

These curves show another characteristic point, which may be designated as the *stiffening point*. This represents the particular temperature at which the test-specimen is deflected 1 mm., *i.e.*, 100 divisions on the scale of the micrometer clock-gauge. At this temperature, the modulus of elasticity is approximately

eight times as great as it is at room temperature. The stiffening point may be regarded as the limiting point at which a rubber mixture is still serviceable.

It is evident from Figure 6, that, with the ordinary type of rubber mixture, the freezing point and stiffening point differ to an extent which depends on the character of the raw material. In addition to this, the temperature differences between the freezing and stiffening points differ greatly. As a rule, with low

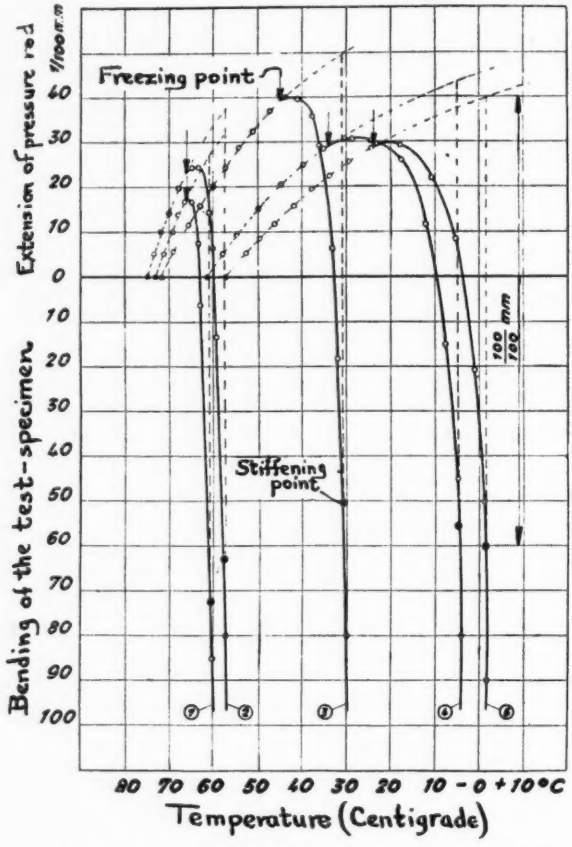

FIG. 6.—Freezing points and stiffening points of some technical mixtures.

(1) Natural Rubber.
(2) Buna-S.
(3) Perbunan.
(4) and (5) Addition of Igelit.

freezing points, these differences amount to 6-8° C; on the other hand they may be 20° C or more in the case of certain cold-resistant materials. In general, Buna-S is about as stable as rubber at low temperatures, although its stiffening point is somewhat higher. Perbunan is considerably poorer than Buna-S, and the addition of Igelit makes Perbunan still less stable at low temperatures.

In the case of mixtures the freezing points of which are not known even in an approximate way, the plunger tube is fixed in its highest possible position (approximately 150 mm.) after being withdrawn from the freezing solution, so

as to avoid lengthening the times of the experiments too much in cases where the freezing points are particularly low. If, in a preliminary experiment, the freezing point turns out to be very high, and the rate of heating consequently is not correctly chosen, the experiment should be repeated with the plunger tube in the position which corresponds to the freezing point. In this way only very small differences in the freezing points will be found.

At this point it is well to mention experiments which led to the adoption of the method of triple loading of the particular weight in deflection measurements at room temperature. This method of loading makes certain the avoidance of an appreciable lag in the softening of a frozen rod test-specimen. The results of

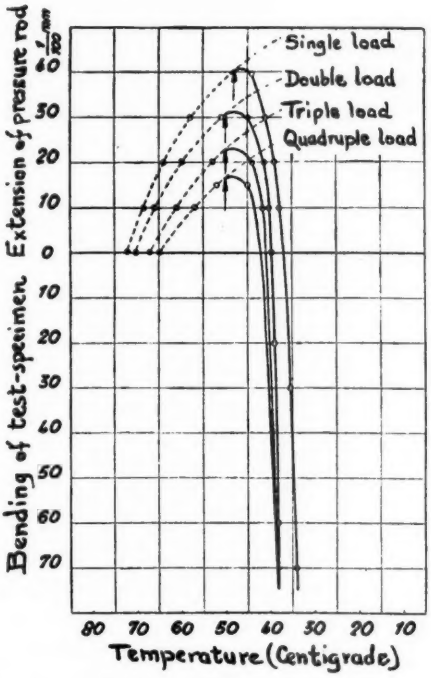

FIG. 7.—Influence of loading on the freezing curve.

these experiments are shown in Figure 7. This particular mixture was loaded successively at room temperature with double, triple and quadruple the specified weight. As was to be expected, both the freezing and stiffening points were a few degrees lower when the single load was applied. The double, triple and quadruple loadings, on the contrary, gave equal freezing points, and the stiffening points too showed practically no differences. To be certain of the results, therefore, the method of triple loading was chosen for determining freezing points.

EXPERIMENTAL PROCEDURE FOR DETERMINING CHANGES IN MODULUS OF ELASTICITY AT DIFFERENT TEMPERATURES

Earlier in this paper, a method for determining the modulus of elasticity at room temperature from the load and deflection of a test-specimen was described.

At subnormal temperatures, the procedure is practically the same as at room temperature. It is necessary, therefore, only to be careful that the temperature around the test-specimen at which the modulus of elasticity is to be determined can be maintained constant for a sufficiently long time. With the apparatus employed in the present work, this requirement was completely fulfilled, for it is safe to assume that the freezing solution was saturated, *i.e.*, that its temper-

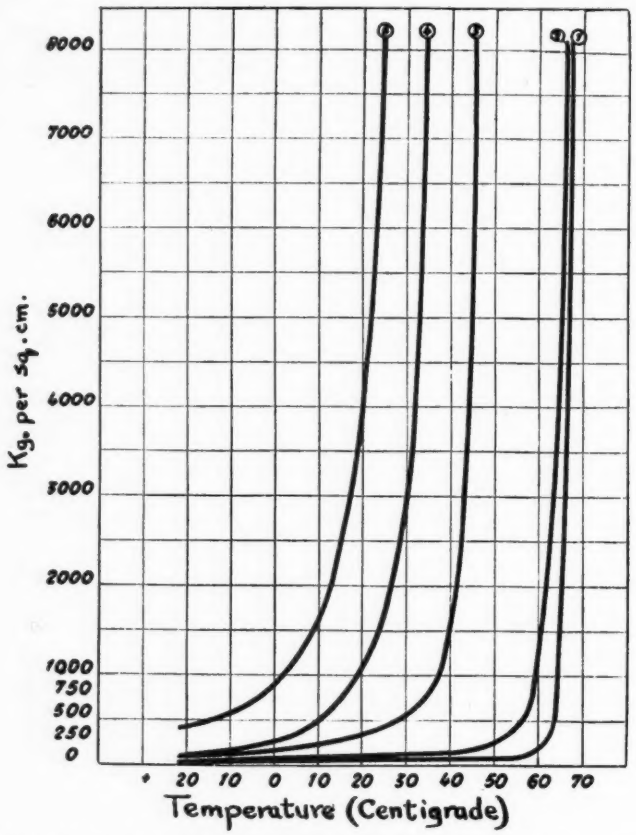

FIG. 8.—Moduli of elasticity of various technical mixtures between 20° C and their freezing points.

ature was −78° C. The different temperatures could be regulated by corresponding adjustments of the plunger tube.

For the apparatus described in the present work, a curve was constructed to show the heights to which the plunger tube should be adjusted. This curve appears in Figure 4 as curve a. When the plunger tube is adjusted by means of this curve, the temperature may be relied on to remain constant for at least ten minutes, whereas a test-specimen reaches the temperature of its surrounding medium within three minutes. The weights chosen for loading a sample are such that the deflection does not exceed 1 millimeter. This weight can be changed from a single loading at room temperature to a triple loading at low temperatures. The deflection is read three seconds after application of the load, and the modulus

of elasticity is calculated by the formula given at the beginning of the present paper.

The data for the mixtures shown in Figure 6 were used to calculate the moduli of elasticity between 0° C and the freezing points, according to the method described. These are shown in Figure 8. The curves are practically the reverse of the curves in Figure 6. Here too, the Buna-S mixture shows a somewhat greater difference in temperature between its freezing point and the increase in its modulus of elasticity than the difference shown by the natural rubber mixture. The Perbunan mixture, and also the same mixture to which Igelit had been

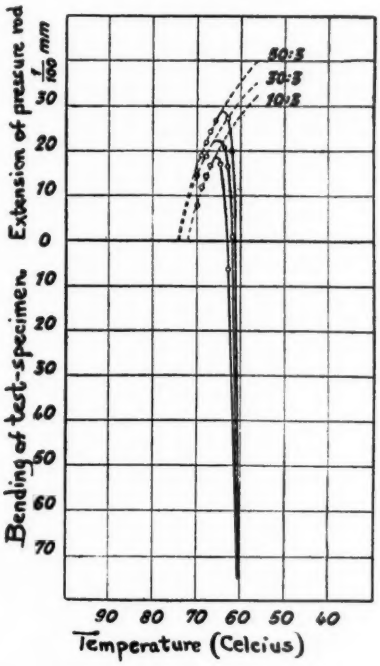

FIG. 9.—Influence of heating on the freezing point.

added, show gradual transitions of the moduli of elasticity at room temperature to those in the neighborhood of the freezing point, as is evident likewise in the curves of Figure 6.

EXPERIMENTAL RESULTS

From a large number of experiments with the various materials described, it is evident that, within certain limits at least, heating does not change to any significant extent the freezing point and stiffening point of a material. It must, however, be emphasized that the changes in stability of the materials at low temperatures as a result of vulcanization have not yet been investigated thoroughly. In the case of an industrial mixture, no change in freezing point or stiffening point was evident within the range of the optimum cure. Increasing degrees of over-vulcanization resulted in only a slight lowering of the freezing point. These experimental results are shown in Figure 9. Furthermore it was

found that, irrespective of the rubberlike materials themselves, the stability of the softening agents which were used in the mixtures had a decisive influence on the freezing points.

SUMMARY

A method for measuring the elastic properties of soft rubber at elevated temperatures and particularly at low temperatures, and for determining its freezing point, is described. This is the first time that a method for testing the flexibility of soft rubber has been used. The special advantages of this method are the small dimensions of the test-specimen and the consequent rapidity with which its temperature can be changed, the small weights with which the test-specimen is loaded, the low heat-capacity of the apparatus, and the ease with which the test-specimen can be made ready for testing. A change of samples can be made within five seconds. The time required for determining the freezing point and hardening point is about one-half hour, after which the apparatus is ready immediately for the next experiment. With a Dewar vessel containing 200-300 grams of solid carbon dioxide, about eight experiments can be carried out without refilling the vessel. Measurements can be reproduced to a fraction of one degree. The factors which, generally speaking, have an influence on the stability of rubber mixtures at low temperatures are discussed. Besides the method for determining freezing points of soft rubber mixtures, a definition of the stiffening point is proposed. Finally the method used for determining the modulus of elasticity of bending is described.

THE KINETICS OF THE POLYMERIZATION OF ISOPRENE ON SODIUM SURFACES *

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INTRODUCTION

In recent years an increasing amount of study has been devoted to gaining a better understanding of the fundamental nature of polymerization reactions. Perhaps the most successful method of approach so far employed has been the systematic study of the kinetics of a wide variety of polymerizations, thermal, catalytic and photochemical. As yet, however, little attention has been directed toward one very important type of polymerization, *viz.*, the polymerization of conjugated compounds in presence of alkali metals. The kinetic method has therefore been applied to the polymerization of isoprene on sodium as a representative example of this class of reactions.

EXPERIMENTAL

The convenient and accurate dilatometric method of following the course of the polymerization was used. From measurements of the limiting value to which the diminution in volume tends on prolonged polymerization, checked by measurements of the density of thoroughly dried polyisoprene, it has been shown that the maximum fractional decrease in volume amounts to 0.25 and is independent of molecular weight, certainly within the limits 3,000-80,000.

The simplest method of preparing a sodium surface on which polymerization might be conducted is undoubtedly by distillation of sodium under high vacuum conditions onto the cool walls of the reaction vessel, which can then be sealed off from the sodium supply. Such films are, however, quite unsuited for kinetic measurements, since their nonuniformity prevents the effective area of the sodium catalyst being estimated with any degree of accuracy. It has, accordingly, been found necessary to conduct experiments on the readily measurable surface area of an appreciable quantity of solid sodium introduced into the reaction vessel by the following method. After thorough evacuation and flaming of the pyrex apparatus sketched (Figure 1), fragments cut from the centre of a large piece of sodium were sealed in. After distillation of the requisite amount of sodium from *A* to *B* and then from *B* to *C* at 10^{-5} mm. pressure, the apparatus was detached from the main vacuum line and immersed in an oil bath at approximately 140° C. The desired amount of purified molten sodium could be poured into the reaction vessel (*D*), which was then sealed off from the remainder. Normally, sufficient sodium was introduced into the reaction vessel to cover the bottom completely, giving a plane surface of area equal to that of the cross-section of the reaction vessel; it was then permissible to eliminate the internal dropper *E*. On certain occasions, however, it was found necessary to introduce only very small globules of sodium. In such cases the internal dropper, *E*, was of value in regulating the amount of sodium transferred to *C*. The by-pass tube

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facilitated evacuation of the sodium during the distillations, and also allowed return of the sodium in *C* if too much had been shaken through the dropper. Using such a technique, it was possible with reasonable certainty to introduce globules of 3 mm. diameter into the reaction vessel. Following the introduction of sodium, the reaction vessel was reattached to the vacuum line, and sealed off at *F* after filling with the required volumes of isoprene and diluent (measured in calibrated side tubes) by liquid air distillation. In certain instances when it was desired to recover unpolymerized isoprene from such reaction vessels, "breakable seals" of the type indicated in Figure 1 (*G*) were attached.

The polymerizations were carried out in 60 and 25° C thermostats, controlled by toluene-mercury regulators to 0.01° C.

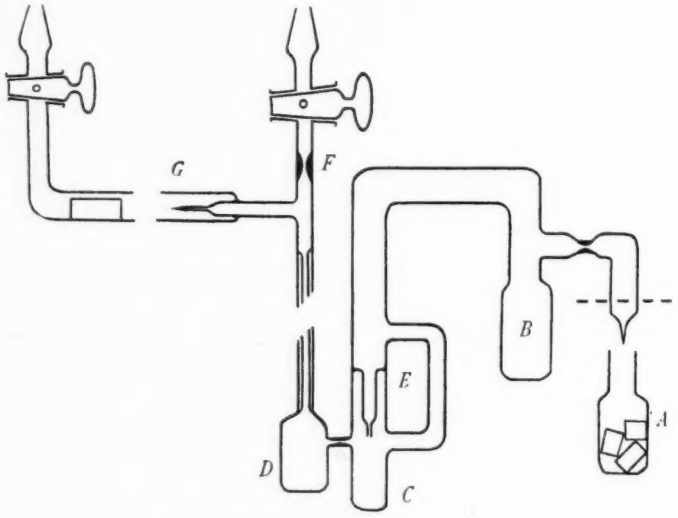

FIG. 1.—Preparation of sodium surfaces.

The molecular weights of the polymers obtained were calculated from measurements of the viscosity of dilute solutions in benzene, using a small volume Ostwald viscometer (flow time for benzene approximately 80 sec.), using the well-known relation:

$$\text{mol. wt} = K \lim_{c \to 0} \frac{\log \eta_r}{c},$$

where η_r represents the relative viscosity of a benzene solution of concentration c (g. per 100 cc. solution). The value adopted for the constant K was 60,000.[1]

Crude isoprene was obtained by the cracking of dipentene, using a modification of Whitby and Crozier's (1932) form of isoprene lamp.[2] The isoprene fraction of the volatile product was converted into the corresponding sulfone, which was twice recrystallized from water, dried and decomposed by heating with caustic alkali. The regenerated isoprene, after washing well with alkali and with water and then drying, was distilled at once over sodium within 1° C range (b.p. 34° C). The yield from the sulfone was 86 per cent. For details of the method of cracking and practical assistance we are indebted to E. H. Farmer.

Of the hydrocarbon diluents employed, the toluene was a B.D.H. sulfur-free product, the benzene was of Analar grade, and the cyclohexane was supplied by B.D.H. as spectroscopically pure. All three solvents were stored in sodium-coated tubes separated from the main vacuum line by taps and mercury cut-offs.

Polymerization of pure isoprene on a clean sodium surface at 60° C is preceded by a short inhibition period, during which no polymerization can be detected, and normally extending to about 30 min., though experience has shown that this period is particularly sensitive to any slight oxidation of the sodium surface. The first visual sign of the commencement of polymerization is the gradual formation of a crimson zone surrounding the contours of the sodium to a depth of approximately 2-3 mm. As polymerization proceeds, it may be shown, by inverting the reaction vessel, that a distinct solid layer consisting of swollen polymer forms round the sodium surface, and this gradually increases in depth till the reaction vessel is completely filled.

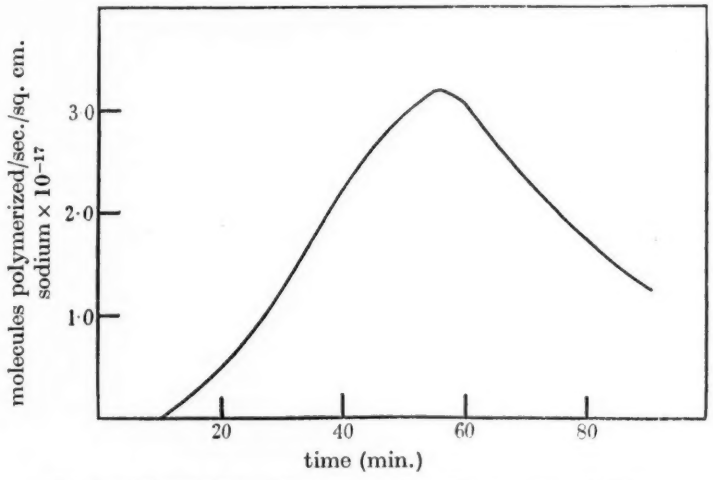

FIG. 2.—Polymerization of isoprene on plane sodium surface at 25° C.

A typical curve representing the progress of polymerization of 100 per cent isoprene on "plane" sodium surfaces at 60° C is given in Figure 2. It is important to note that the curve shows a relatively sharp maximum. From visual estimates of the thickness of the polymer layer at somewhat later stages in the polymerization, it is estimated that the maximum rate of polymerization occurred when a layer of approximately 6 mm. had been formed on the surface.

KINETICS OF POLYMERIZATION IN PRESENCE OF TOLUENE

The kinetic data obtained when polymerization runs are carried out in presence of added amounts of toluene on plane sodium surfaces give, in the main, curves of the type indicated in Figure 2. The variation of the maximum rate of polymerization at 60° C with the amount of toluene added is as indicated by the data given in Table I.

It is noteworthy that, while the addition of 35 molar per cent of toluene reduces the molecular weight of the polyisoprene by a factor of approximately 4,

the maximum rate of polymerization is diminished by only 36 per cent under such a change of conditions. Polymerization runs, in which sodium surfaces of various configurations were used, have shown that this lack of correlation between the rate of polymerization and the chain length of the polymer produced resulted from the fact that the diffusion of the monomer through the intervening polymer layer to the site of reaction was the factor determining the observed rate of polymerization. The details of these experiments, and the maximum rates of polymerization measured, are given in Table II, the course of the runs is indicated graphically in Figure 3.

Provided the extent of the induction period depends on characteristics of the surface and not on those of the liquid, it can be shown that the probability of observing the complete course of the induction period, before diffusion becomes the rate-controlling factor, is much increased by the use of curved surfaces. Thus in Figure 4 curves have been constructed relating the rate of diffusion

TABLE I

Molar percentage toluene	Maximum rate of polymerization (molecules polymerized per sec. per sq. cm. sodium $\times 10^{-17}$)	Molecular weight
4.65	3.24	80,000
5.7	3.18	84,000
8.61	3.23	70,000
10.7	2.65	59,500
17.7	2.02	31,200
35.0	2.0	20,600
48.5	1.08	10,800
65.9	0.32	3,800

(to unit surface area) with extent of reaction (per unit area) based on the following equations, which are derived on the assumption that Fick's law holds:

$$\text{for a plane surface: } \frac{\text{rate of diffusion}}{\text{unit area}} = \frac{D\Delta C}{t},$$

where t is the thickness of polymer layer, D the diffusion coefficient and ΔC the difference in monomer concentrations at the polymer-liquid and polymer sodium interfaces;

$$\text{for spherical surfaces: } \frac{\text{rate of diffusion}}{\text{unit area}} = \frac{D\Delta C}{r_1(1-r_1/r_2)}, \qquad (1)$$

where r_1 and r_2 are respectively the radii of curvature of the surface and the polymer-liquid interface.

The fact that the observed maximum rate of polymerization is increased by the use of spherical sodium surfaces demonstrates the existence of the diffusion effect, while the stationary nature of the maximum rate in the case of the smaller hemispherical surface indicates that the true maximum rate of polymerization was attained before the rate of diffusion became the rate-controlling factor.

That the maximum rate of polymerization observed on surface (*c*) should be uninfluenced by diffusion seems reasonable and can be shown as follows. The maximum rate is attained when 1.16 cc. (dry) polymer have been formed. Swelling measurements show that polyisoprene swells to twice its volume in presence of isoprene at 60° C. Allowing for this factor, it can be shown that

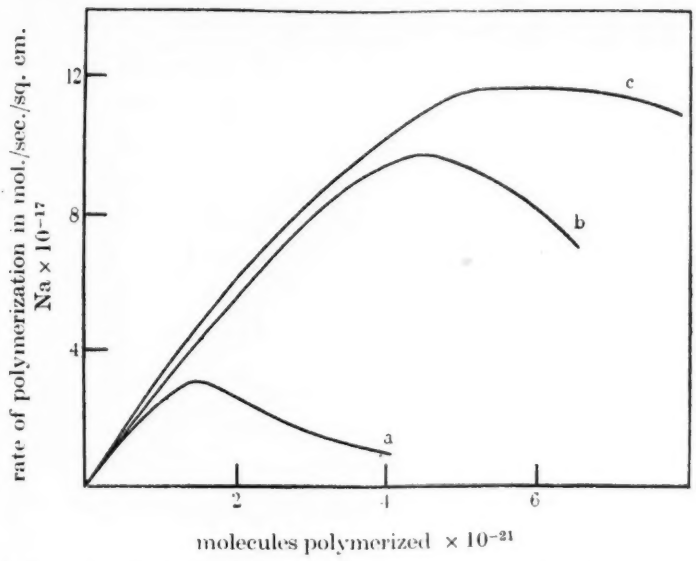

FIG. 3.—Polymerization of isoprene at 25° C on (*a*) a plane sodium surface, and hemispherical surfaces of radii, (*b*) 0.20 cm., and (*c*) 0.14$_7$ cm.

TABLE II

POLYMERIZATION OF ISOPRENE + 8.61 MOLAR PER CENT TOLUENE AT 60° C

Description of surface	Maximum rate of polymerization (molecules per sec. per sq. cm. sodium $\times 10^{-17}$)
(*a*) Plane	3.2$_3$
(*b*) Hemispherical, $r_1 = 0.20$ cm	9.7
(*c*) Hemispherical, $r_1 = 0.14_7$ cm	11.0

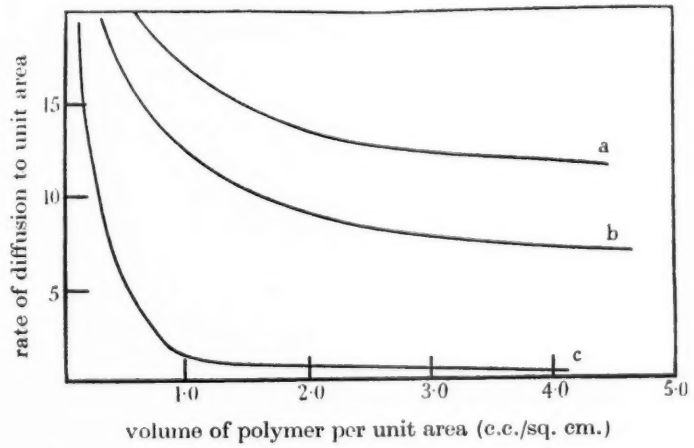

FIG. 4.—Diffusion of isoprene to sodium surfaces of various shapes: (*a*) hemisphere of radius 0.10 cm., (*b*) hemisphere of radius 0.15 cm., and (*c*) plane surface.

the radius of curvature (r_2) of the polymer liquid phase interface (assumed hemispherical, since the radius of curvature of the sodium surface was much smaller than the cross-sectional diameter of the reaction vessel) is 10.5 mm. when the maximum rate of polymerization is attained. Inserting the relevant values in Equation (1), $D\Delta C$ is found to be 2.1×10^{17} mol. per sec. per cm. Unfortunately, the value of D for this actual system has not been measured; Abkin and Medvedev[3] have, however, determined the same quantity for the very similar system butadiene-polybutadiene, and extrapolation of their results would indicate a value of approximately 1.5×10^{-3} cm.^{2} sec.$^{-1}$ at 60° C. If this value is applied to the present case, $\Delta C=1.4\times10^{20}$ mol. per cc. The saturation concentration—that at the polymer-liquid boundary—is estimated at 3.0×10^{21} mol. per cc., on the grounds that isoprene swells the polymer to twice its normal size, with little total volume change. In this case, then, it seems reasonable to assume that the monomer concentration in the neighborhood of the sodium is but little removed from the saturation concentration.

TABLE III

Toluene concentration (molar percentage)	Isoprene concentration / Toluene concentration	Maximum rate of polymerization (molecules per sec. per sq. cm. sodium $\times 10^{-17}$)	Chain length	$K\times10^{-17}$	K_1
2.90	29.9	32.5	—	1.06	—
8.61	9.40	11.0	1780	1.17	189
22.9	3.37	4.0	580	1.19	172
35.0	1.86	2.0	330	1.07	177
48.5	1.06	1.08	156	1.02	148
65.9	0.36	0.32	56	1.89	175
			Mean	1.07	172

K and K_1 are constants defined by Equations (2) and (3) below.

By conducting polymerizations on hemispherical sodium surfaces of sufficiently small dimensions, it has been found possible to determine the true maximum rate of polymerization over substantially the whole range of toluene concentrations. These results are incorporated in Table III.

It is evident from Table III that the maximum rate of polymerization is related to the concentrations of isoprene and toluene by the following simple relationship:

$$R_{max}=K\frac{[\text{isoprene}]}{[\text{toluene}]}. \tag{2}$$

The mean chain lengths of the polymers obtained in these experiments are also included in Table III, and it is evident that a parallel relationship exists between the chain length and the isoprene concentration, *viz.*:

$$\text{chain length}=K_1\frac{[\text{isoprene}]}{[\text{toluene}]}. \tag{3}$$

A similar series of experiments performed at 25° C, using hemispherical beads where necessary, yielded quite analogous results, although here it was unfortunately not found possible to extend the measurement of true maximum rates of polymerization to quite such high isoprene concentrations. The data are given in Table IV.

POLYMERIZATION OF UNDILUTED ISOPRENE

Examination of the polymer obtained by polymerizing undiluted isoprene shows that the larger portion of it is quite insoluble in benzene. Thus, in one typical instance a sample mechanically shaken with benzene for about 30 days in a tube which had previously been carefully evacuated gave an insoluble residue amounting to 65 per cent by weight; the mean molecular weight of the soluble portion was found to be 210,000. Further shaking of the portion insoluble in benzene with 10 per cent ethyl alcohol in benzene resulted in no further solution being effected. As in the case of reaction mixtures containing toluene, the observed maximum rate of polymerization was very markedly increased by substitution of hemispherical for plane sodium surfaces. It was never found practicable, however, to prepare a surface of sufficiently small dimensions to allow for observation of a rate of polymerization greater than 1.66×10^{18} molecules per sec. per sq. cm.; in this particular run there was no appreciable interval following attainment of the maximum rate of polymerization during which the rate of polymerization remained constant. The conclusion is, there-

TABLE IV

Toulene concentration (molar percentage)	Isoprene / Toluene	Maximum rate of polymerization (molecules per sec. per sq. cm. sodium $\times 10^{-17}$)	Chain length	$K \times 10^{-16}$	K_1
8.6	9.4	1.48	2720	1.58	290
25.6	2.92	0.49	880	1.68	320
45.7	1.19	0.17_5	412	1.47	346
63.7	0.57	0.10_8	188	1.89	303
			Mean	1.65	315

fore, that the true rate of polymerization of 100 per cent isoprene exceeds 1.66×10^{18} molecules per sec. per sq. cm. (It will be noted that in one case (see Table III) a higher rate of polymerization has been measured: conditions were specially favorable in that particular run, since the diameter of the bead was only 2.0_4 mm., compared with the 3.0 mm. for the second smallest bead prepared during these experiments and, moreover, the isoprene was derived from a sample which had previously been partly polymerized; there is good reason to believe that this latter factor should have diminished the extent of the induction period.)

NATURE OF INDUCTION PERIOD

It seems almost certain that the induction period observed in the polymerization reaction under consideration must arise from one of two possible causes. The induction period may represent the time taken for the establishment of the maximum (stationary) number of centres from which polymerization may proceed or, alternatively, the period during which are destroyed adventitious impurities in the isoprene (or solvents), which may inhibit the initiation of polymerization chains, or by their interaction bring polymerization chains to a premature termination.

A series of experiments, in which the polymerization of 100 per cent isoprene on plane sodium surfaces was interrupted at some point during the induction period, showed that the molecular weight of the polymer formed during the

induction period is quite significantly lower than that of the soluble portion of the polymer obtained from completed reactions:

Molecules of isoprene polymerized at interruption per sq. cm. sodium $\times 10^{-19}$	Molecular weight
7.5	5,800
17.5	14,600
23.5	24,000
27.1	13,400
165	48,000

(The maximum rate of polymerization on a plane surface occurs after polymerization of approximately 180×10^{19} molecules per sq. cm.)

While these figures are not very concordant among themselves, they indicate that the molecular weight gradually increases throughout the induction period to a value which is still significantly smaller than the final mean molecular weight of the soluble portion of the polymer. To decide whether the induction period and (or) this initial depression of the molecular weight were due to the presence of a trace of some efficient chain terminator, a 6-cc. sample of isoprene was subjected to a series of successive partial polymerizations. The reaction vessels used for this purpose were provided with breakable seals (Figure 1 (*G*)). On attainment of the maximum rate of polymerization, the remaining unpolymerized isoprene was transferred to a similar reaction vessel via the breakable seal. Benzene was then distilled into the first reaction vessel in sufficient quantity to effect the solution of the polymer (carried out *in vacuo*). This cycle was carried out four times with the results shown in Table V.

As is evident from Table V, with each partial polymerization the mean chain length during the induction period shows an undoubted upward trend, while the induction period becomes shorter and shorter. We conclude that a contributory factor to the induction period is the presence of adventitious traces of impurity in the isoprene, even when purified with extreme care. It was observed that, while the initial stages of the first polymerization of the above series were accompanied by the development of the (normal) crimson coloration near to the surface, in the subsequent runs such coloration was quite absent. In view of the observations made by L'vov[4] that the products resulting from the copolymerization of butadiene and isobutylene in presence of sodium were of an intense cherry red color (and extremely sensitive to the influence of moisture and air) and, also, that the presence of isobutylene has a marked effect in reducing the chain length of sodium-catalyzed polyisobutadienes, it seems likely that the impurity concerned is in fact a monoölefine.

The last two experiments included in Table V represent an attempt to detect whether the addition of monomer molecules to polymer chains is a relatively slow process (of the type suggested for the photochemically initiated polymerization of methyl methacrylate,[5] so that the completion of a polymer chain might occupy several minutes. Run V, using isoprene from run IV, served as a control, conducted similarly to the previous four experiments. In the case of run VI, using the ioprene recovered from V, the reaction was interrupted at the same stage (measured by the contraction) and, by inverting the reaction vessel, it was arranged that the polymer already formed should have an opportunity of continuing growth in absence of sodium. The extent of reaction permitted on the catalytic surface was regulated so that it was still possible to disperse the polymer quite rapidly in the remaining isoprene by manual shaking. On leaving

the inverted reaction vessel at the previous polymerization temperature (60° C) for 24 hours, the remaining isoprene was found to have polymerized on the sodium surface, while, as will be seen from Table V, the polymer removed from the catalytic surface did not undergo any further growth. It is unfortunate that the insoluble nature of the polymer formed subsequent to the completion of the induction period (when it could be assumed that all adventitious chain terminators would have been eliminated) prevents repetition of such experiments during the later stages of the polymerization.

It is to be noted that the results presented in Table V cannot well be explained completely in terms of the presence of adventitious inhibitors. Thus it was found that only 35 per cent of samples of polyisoprene obtained by complete polymerization of undiluted isoprene was soluble in benzene. It is to be supposed that the soluble portion resulted from the early stages of the polymerization, owing to the interaction of inhibitors, and any possible premature chain terminating effect due to the state of the surface. Assuming for the moment that the predominating factor is the presence of inhibitors, each molecule of

TABLE V

(TEMPERATURE = 60° C)

	Volume of isoprene used (cc.)	Volume of isoprene recovered (cc.)	Chain length	Maximum rate of polymerization (molecules per sec. per sq. cm. sodium $\times 10^{-17}$)	$P \times 10^{-21}$
I	5.10	4.37	705	3.55	1.69
II	3.94	2.16	1160	3.87	1.25
III	2.16	1.70	1330	4.28	0.93
IV	1.56	1.23	1690	4.44	0.57
V	1.08	0.93	425	—	—
VI	0.93	—	398	—	—

P represents the number of molecules of isoprene polymerized at the point when the maximum rate of polymerization is attained.

which terminates one chain only, it follows from the molecular weight of the soluble portion (210,000) that the concentration of inhibitor is 1.3×10^{-2} molar per cent. On the other hand, by polymerizing a sample of isoprene in successive stages (as in Table V), it is possible to obtain from it at least 70 per cent soluble polymer of mean molecular weight 73,000, corresponding to an inhibitor concentration of 6.5×10^{-2} molar per cent. It must, therefore, be supposed that an additional contributory factor is in operation in determining the molecular weight during the early stages of polymerization. Since the care taken in preparing the catalytic surfaces should rule out the presence of possible inhibitors on the sodium surface, it would seem that the effect must be due to some more fundamental characteristic of the sodium surface during the induction period.

POLYMERIZATION OF ISOPRENE VAPOR ON SODIUM

It is well known that conjugated substances readily polymerize on sodium, even when their vapor pressure is much less than the saturation value. A system of this type is more suitable for kinetical study than the corresponding liquid system, since the effective monomer concentration may be readily altered without introducing diluents which may well have a complicating effect on the kinetics. Moreover, an additional advantage accrued in the case of isoprene,

since, in distinction to the liquid phase reaction, a stationary maximum rate of polymerization was observed in absence of toluene.

The apparatus employed consisted of a suitable reaction vessel, around which water at 25 or 60° C could be circulated, attached to a constant pressure gas burrette of the normal type. The burette was controlled manually, variations from the initial pressure being observed through a telescope focussed on the meniscus of a wide-limbed mercury differential manometer. Sodium films were deposited on the walls of the reaction vessels in two ways: thicker sodium films were introduced by distillation from a side tube which was then sealed off, while small yet measured amounts of sodium were in some instances introduced, using the method described by Burt[6], whereby sodium could be electrolyzed through the soda glass walls of the reaction vessel; the strength and duration of the electrolytic current gave an accurate estimate of the amount of sodium introduced in this way.

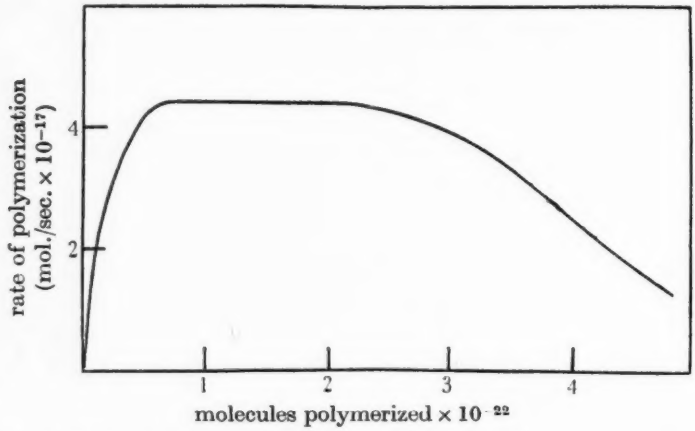

FIG. 5.—Polymerization of isoprene vapor (p = 380 mm. of Hg) on a thin sodium surface at 25° C.

Figure 5 represents the course of a polymerization carried out on a thin film of sodium, consisting of 1.12 mg. introduced electrolytically. The temperature was 25° C, and the vapor pressure of isoprene approximately 370 mm. It will be noted that the rate of polymerization gradually reaches a maximum value, which is maintained for some time before finally diminishing again.

A few experiments carried out on thicker sodium films yielded results the general nature of which agree well with those obtained by Abkin and Medvedev[3, 7] from a careful study of the analogous butadiene reaction. They may be summarized as follows. The rates of reaction in the pressure range 100-350 mm., measured on one particular sodium surface following the completion of the induction period, were found to conform to the following expressions:

$$\text{at } 25^\circ \text{ C}, R = 5.80 \times 10^{10} p^{2.7} \text{ mol. per sec.},$$

and

$$\text{at } 60^\circ \text{ C}, R = 3.85 \times 10^{13} p^{1.4} \text{ mol. per sec.},$$

where p is the gas phase pressure of isoprene in mm. of Hg. The absorption isotherms of isoprene on the polymer which had previously been allowed pro-

longed exposure to oxygen were determined over the same pressure range and found to approximate to the forms:

$$\text{at } 25^\circ \text{ C: } C = 1.52 \times 10^{14} p^{2.5},$$

and

$$\text{at } 60^\circ \text{ C: } C = 3.00 \times 10^{16} p^{1.25},$$

where C represents the concentration of isoprene in the polymer in mol. per cc.

These empirical relations yield the following expressions for the rate of polymerization in terms of the isoprene concentration:

$$\text{at } 25^\circ \text{ C: } R = 2.50 \times 10^{-5} C^{1.08} \text{ mol. per sec.}$$

and

$$\text{at } 60^\circ \text{ C: } R = 1.35 \times 10^{-5} C^{1.12} \text{ mol. per sec.}$$

in agreement with the first order nature of the analogous butadiene reaction, as found by Abkin and Medvedev.

In the concentration range common to the measurements at 60 and 25° C (*viz.*, 1.5×10^{19} to 6.0×10^{19} mol. per cc. of polymer), the ratio of the rates of polymerization (at equal monomer concentrations) has a mean value of 3.08, corresponding to an activation energy of 6.4 kcal.; the figure is similar to the activation energy of the butadiene polymerization obtained by Abkin and Medvedev, *viz.*, 7.3 kcal.

INTERPRETATION OF KINETIC DATA

There is no reason to suppose that the polymerization of isoprene on sodium departs from the generally recognized view that such reactions are of a chain character, involving three distinct phases, namely, initiation, propagation and termination of the chains. It will be convenient to consider in that order the nature of these three processes in the light of the information outlined above.

It has been shown that the kinetic data relating to the polymerization of liquid isoprene suggest the validity of the equations:

$$R = K \frac{[I]}{[T]}, \tag{2'}$$

and

$$\nu = K_1 \frac{[I]}{[T]}, \tag{3'}$$

where R and ν represent the rate of polymerization and the chain length of the polymer formed: $[I]$ and $[T]$ refer to the concentrations of isoprene and toluene. It is evident from these equations that the rate of initiation of chains ($=R/\nu$) is independent of isoprene or toluene concentrations. Assuming the zero order nature of the initiation process, it can readily be shown by the normal stationary state procedure that the only type of terminating reaction consistent with Equation (2') involves the interaction of the active propagating centre with toluene.

NATURE OF INITIATION REACTION

The various possible alternatives may, in the first place, be classified according to whether or not the initiation process involves the irreversible incorporation of sodium into the chain centre. Incineration of samples of polyisoprene, obtained from the polymerization of 100 per cent isoprene and of isoprene mixed

with an equal proportion of toluene, failed to reveal the presence of even traces of sodium in the polymer. In the latter case the detection of sodium should have been extremely easy, since the incineration of the 1 gram of sample would have yielded 0.01 gram of sodium sulfate for each sodium atom incorporated per polyisoprene molecule. It must, accordingly, be assumed that the reaction mechanism is such that at no stage is sodium incorporated in the polymer chain. Some confirmation of the absence of sodium in the finished polymer arises from the experiment mentioned above, in which polymerization was carried out on 1.12 mg. of sodium at 25° C. During this reaction, 12 grams of isoprene were polymerized, without the sodium deposit showing any marked decrease in size or density. It is to be noted that, even if all the sodium were incorporated in the polymer so that each polymer chain contained one sodium atom, the molecular weight would be 250,000.

This evidence conflicts with the views of Abkin and Medvedev[3, 7] regarding the mechanism of the polymerization of butadiene vapor on sodium. They conclude that the initiation reaction consists of the formation of definite disodium complexes of the type:

$$Na-CH_2-CH=CH-CH_2-Na,$$

the chain growth thereafter occurring by successive insertions of manomeric molecules between one of the sodium atoms and the hydrocarbon portion of the complex. As no termination reaction is specifically mentioned, this mechanism would lead to the expectation that the finished polymer would contain two sodium atoms per molecule.

From the experimental data available, it is possible to estimate the activation energy required in the initiation process. The overall activation energy of the polymerization (ΔE) may be resolved into three components, representing the activation energies associated, respectively, with the initiation (ΔE_i), the propagation (ΔE_p), and the termination processes (ΔE_t), thus:

$$\Delta E=\Delta E_i+\Delta E_p-E_t.$$

ΔE can readily be calculated as 11.0 kcal. from the variation of the quantity K with temperature (Tables III and IV), while the temperature variation of K_1 (Tables III and IV) yields a value for ($\Delta E_p-\Delta E_t$) of −3.4 kcal. The activation energy of the initiation reaction is, accordingly, 14.4 kcal.

The initiation reaction is almost certainly in itself a composite reaction, consisting of three possible consecutive phases: the adsorption of an isoprene molecule to the neighborhood of the sodium surface, any activation on the surface, and possibly desorption of the activated complex so formed. The activation energy measured corresponds to the slowest process. It is unfortunate that no detailed study of the adsorption of conjugated hydrocarbons on alkali metals has been made, with the result that no decision has been reached as to the mode of adsorption involved. There seem good grounds for supposing that the chemisorption of isoprene concerns the attachment of the isoprene in the form:

$$-CH_2-CH=\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}-CH_2-$$

to the positive ions forming the sodium crystalline lattice. From a consideration of the mutual forces between the isoprene molecule and sodium ion, it must be

supposed that the maximum value of the activation energy required for the formation of such an adsorption complex would be the resonance energy of the isoprene molecule. While this quantity has not been determined, it should not vary greatly from the figure of 5 kcal. obtained by theoretical and experimental methods for the butadiene molecule[8]. It may be concluded therefore that the activation of the isoprene at the catalytic surface is not the rate-determining factor.

It is therefore necessary to identify the 14.4 kcal. energy with a desorption process, involving the cleavage of a carbon-sodium linkage. Two alternative mechanisms which include such a step must be considered: in the first, the adsorbed isoprene molecule leaves the catalytic surface in active form, the chain propagation occurring thereafter away from the sodium surface; the second alternative is that the chain growth of each polymer molecule occurs while the molecule is still attached to the catalytic surface by the original carbon-sodium linkage, desorption of the finished polymer molecule occurring at some time subsequent to the termination of the chain growth. In both cases the factor controlling the rate of initiation is thus in effect the rate at which sites on the catalytic surface are vacated. In view of the experimental fact that the rate of initiation is independent of isoprene (and toluene) concentration, it is necessary to suppose that in the first case in the concentration range examined the catalytic surface is always saturated with isoprene molecules, while in the second case the additional assumption must be made that the termination of the chain growth is no way affects the lifetime of the polymer molecule adsorbed on the surface. Although there is no readily apparent method of deciding experimentally between these alternatives, it is felt that the adsorption complex: $Na-CH_2-CH=CH-CH_2-$, represents a more likely initiation centre than a desorbed isoprene molecule, which would so readily revert to its stable configuration.

NATURE OF PROPAGATION REACTION

In view of the conclusions drawn as to the nature of the initiation reaction, it follows that the propagation reaction must be of the free radical type. Evidence has been provided[9] that conjugated molecules may become incorporated in polymer chains in the 1-2 sense, *e.g.*:

$$\ldots-CH_2-\underset{\displaystyle CH \\ \displaystyle \| \\ \displaystyle CH_2}{CH}-\ldots$$

as well as in the 1-4 sense, *e.g.*, $\ldots-CH_2-CH=CH-CH_2-\ldots$. That both modes of addition are in operation in the present case also has been suggested by x-ray observations carried out by G. A. Jeffrey. Polyisoprene samples, both in the unstretched and stretched condition, failed to give any indication of the x-ray phenomena associated in the case of rubber with regularity of structure. The possibility that the lack of structure was attributable to the irregular distribution of isoprene units orientated in the two possible ways:

$$-CH_2-\underset{\displaystyle CH_3}{C}=\underset{\displaystyle H}{C}-CH_2- \qquad \text{and} \qquad -CH_2-\underset{\displaystyle H}{C}=\underset{\displaystyle CH_3}{C}-CH_2-$$

was eliminated by submitting a sample of polybutadiene—prepared under the same conditions as the polyisoprene—to x-ray examination. Since, in this case also, no evidence of regularity of structure could be obtained, it must be assumed that both modes of polymerization, 1-2 and 1-4, do actually occur.

NATURE OF TERMINATION REACTION

There is good reason to suppose that toluene acts as an effective terminating agent through chemical interaction with the centre of growth, as distinct from the physical interaction normally associated with "solvent action", since it was found that addition of cyclohexane produced no appreciable effect on the polyisoprene formed. Thus in one instance, in which 38 molar per cent cyclohexane was added to the isoprene, the polymer obtained at 60° C was only 30 per cent soluble; the molecular weight of the soluble portion being 217,000, in excellent agreement with the data obtained for polymers obtained from undiluted isoprene. Benzene, on the other hand, produces an effect comparable with that of toluene: in one experiment at 60° C, using 46.7 molar per cent benzene, the maximum rate of polymerization (and judging from the fact that the maximum rate of polymerization was maintained for a considerable portion of the reaction it represented the true maximum rate of polymerization) was 2.1×10^{17} molecules per sec. per sq. cm. and the mean chain length was 530. This would indicate that the rate of production of initiation centres was 4.0×10^{14} per sec.—a figure in reasonable agreement with that obtained in presence of toluene, *viz.*, 6.5×10^{14}. From the ratio of molecular weights obtained under equal molar concentrations of toluene and benzene, it can be deduced that the termination reaction involving toluene is some 3.6 times more efficient than that involving benzene.

The kinetic evidence shows that, even where only 2.9 molar per cent toluene is present, the termination of polymer chains is wholly effected by toluene: this is also in agreement with the complete solubility of the polymer obtained at such low toluene concentrations—contrasted with the partial insolubility of the polymer obtained when no toluene is present. In absence of toluene, therefore, an alternative termination mechanism—the efficiency of which is considerably less than that involving toluene—must come into play. The onset of insolubility may be due to one of two characteristics of the additional termination mechanism; the deactivation of each growing chain may be accomplished by interaction with points in other polymer molecules which are of abnormal chemical activity (*e.g.*, pendant vinyl groups formed, when propagation of the polymer chain occurred by 1-2 addition), thus producing a net or cross linked structure; alternatively, the efficiency of the terminating reaction may be so small that the polymer becomes of such dimensions as to become inextricably entangled with other polymer molecules, even in the presence of solvent. This latter condition would give rise to an almost infinitely great rate of polymerization but, since even the highest rate of polymerization observed experimentally appeared to be controlled by the rate of diffusion, there are no experimental grounds for dismissing this possibility. It is, however, rendered less likely by the observation of Bronsted and Volqvartz[10] that polystyrenes of molecular weight of the order of 1,000,000 could be dissolved in benzene.

Polymers of similar insolubility are obtained when isoprene at pressures below the saturation vapor pressure is allowed to polymerize on sodium surfaces. It is reasonable to suppose that the nature and energetics of the initiation, propagation and termination reactions concerned in this "gas phase" polymerization are

identical with those of the corresponding reactions involved in the later stages of the polymerization of undiluted liquid isoprene. From the fact that a stationary maximum rate of polymerization is established in the case of the "gas-phase" reaction, it must be assumed that a termination reaction is in operation. To explain the overall energy of activation of the liquid phase reaction being some 4.6 kcal. greater than that of the gas phase reaction, it is necessary to suppose that the termination reaction, which produces insolubility, requires 4.6 kcal. greater activation energy than the termination reaction involving toluene.

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MIXED POLYMERS AND VULCANIZABLE PLASTICIZERS

RELATION TO THE VULCANIZATION OF RUBBER *

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The vital role played by rubber in modern civilization is due in part to the physical properties displayed by soft vulcanized rubber in service and in part to the characteristics of unvulcanized milled rubber which make it amenable to manufacturing operations. Vulcanization of rubber is a change in condition usually induced by heating it with sulfur, and is best defined by contrasting the difference in physical properties:

Unvulcanized rubber		Vulcanized rubber
Low tensile strength		High tensile strength
Limited elasticity		Extensive elasticity
Low recovery		High recovery
High retentivity		Low retentivity
High flow		Low flow
Narrow temperature range	Vulcanization →	Wide temperature range
Plasticity		Nonplasticity
Thermoplasticity		Nonthermoplasticity
Solubility		Lack of solubility
Tackiness		Lack of tackiness

To illustrate, compare a mill-mixed composition before and after vulcanization. Before vulcanization it is easily pulled apart and, if considerably extended, shows little tendency to retract, although, under impact, the recovery or rebound is considerable. If heated it becomes even softer and more plastic, and can easily be formed into any desired shape. If cooled to 0° C or somewhat lower, it becomes stiff and boardy. It is readily soluble in hydrocarbon solvents. When two fresh surfaces are pressed together, they coalesce and become practically integral. This tack, as it is called, is valuable in manufacturing operations.

After vulcanization, rubber is tough and strong and, after even a slow distortion, returns rapidly to its original shape. It has little tendency to flow and is devoid of tack. It swells but does not dissolve in hydrocarbon solvents. These characteristics change very little from −40° to well above 100° C.

This comparison shows that the useful, elastic character of rubber is developed during vulcanization. It is obviously desirable to know what chemical transformation is responsible for these changes in physical properties or, at least, what type of chemical change can produce them.

The direct attack is difficult because rubber and its solutions are inherently unsuited to ordinary chemical methods of manipulation and because the number of reactions which can take place in a single rubber molecule makes it impossible

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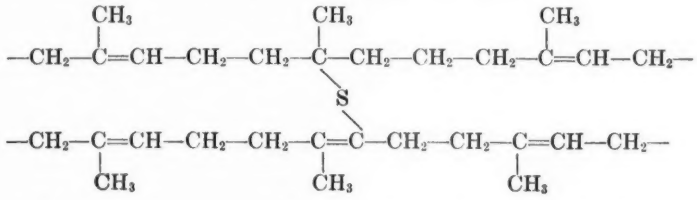
to separate the various products of simultaneous reactions without complete breakdown of the product.

Several years ago a few physicists and physical chemists were advancing general ideas relative to the structure and elasticity of elastic products, especially rubber. [Since those articles[1, 2, 10, 11, 14] were published, several books have appeared with summaries of the theories expressed in them[3, 9, 13].] According to these views, during vulcanization the molecules of unvulcanized rubber, consisting of long primary valence chains of isopentene groups, are bound together at various places by sulfur bridges. One possibility is the following:



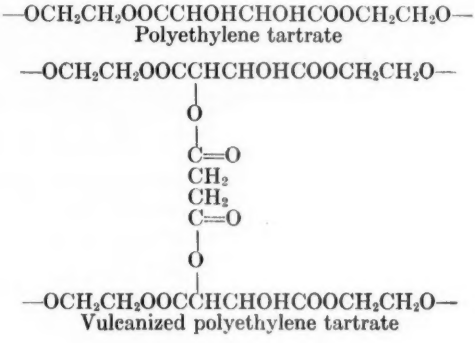
This sulfur bridge is an example of a chemical cross-bond. It may also be considered as a fixed point, since at this place the two molecules are held in fixed positions relative to each other, whereas at other places the two molecules are relatively independent of each other and are continually shifting under the influence of thermal agitation.

If the establishment of chemical cross-bonds in unvulcanized rubber leads to vulcanization and the formation of elastic products, chemical cross-bonds might have a similar effect in nonrubber systems. The object of the first experiments with other systems was to check the effect of chemical cross-bonds on physical properties.

FORMATION OF CHEMICAL CROSS-BONDS BY CONDENSATION

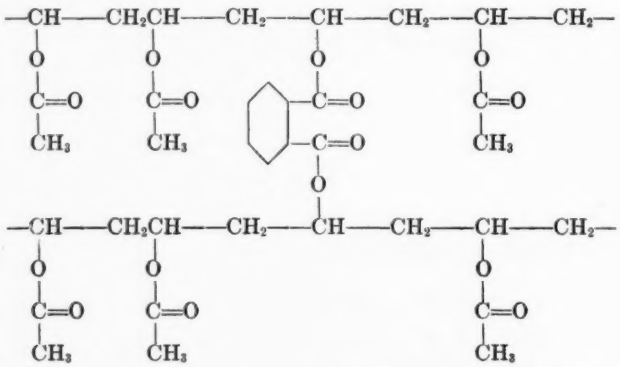
Polytartrates.—Polyethylene tartrate was prepared by ester interchange between diethyl tartrate and ethylene glycol. It was a glassy resin which melted to a viscous liquid at elevated temperatures. When this liquid was heated with succinic acid, water was evolved and the liquid gelled to a spongy, resilient material, which became hard on cooling. When reheated, it again became elastic rather than plastic. Whereas the polyethylene tartrate was thermoplastic, the vulcanized product was thermoelastic.

The probable structures of these two products are as follows:



Similar products were obtained by making the polysuccinate of tartaric acid and "vulcanizing" it with ethylene glycol.

Polyvinyl acetate and diethyl phthalate.—Diethyl phthalate is a fairly good plasticizer for polyvinyl acetate. When 2 moles of polyvinyl acetate were heated with 1 mole of diethyl phthalate at 280° C, the mixture was at first a viscous liquid. As heating was continued, however, ester interchange took place and the product gelled. The reaction did not go to completion, and much of the diethyl phthalate was left as a plasticizer. At room temperature the product was weak and somewhat elastic. At 120° C it was elastic rather than plastic, but was sluggish in recovery, and had low tensile strength and a short break. It probably has the following structure:

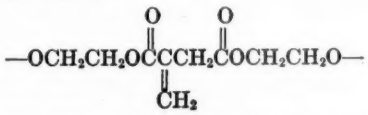


A more completely vulcanized product was obtained by reacting ethylene glycol with succinic acid to make polyethylene succinate, which was then heated further with polyvinyl acetate. The polyethylene succinate was a good solvent for the polyvinyl acetate and the unreacted succinic acid. When heating was continued for a sufficient time, the product became tightly gelled and elastic. It cooled to a fairly hard elastic product which was largely insoluble in benzene and acetone. (In this work we had also hoped to obtain chemically bound plasticizers. If only one of the ester groups of the diethyl phthalate reacted, the rest of the molecule would be left as a plasticizer which could not be extracted by solvents. Such products have been obtained in the cellulose acetate-butyrate and various copolymers.) In these experiments the vulcanizing reaction was an esterification or an ester interchange, involving the liberation of a volatile material. This volatile material vaporized and formed blown and porous products. When pressure was applied to prevent blowing, the reaction did not proceed satisfactorily because it depends on the escape of the volatile material to shift the equilibrium. It was concluded that a satisfactory vulcanizing reaction should not form any volatile product.

CHEMICAL CROSS-BONDS BY ADDITION POLYMERIZATION

In the vulcanization of polyvinyl acetate with diethyl phthalate, the order of procedure was: (1) polymerization to a chain polymer; (2) ester interchange to form cross-bonds. Because of the trouble with blowing, the second reaction is less satisfactory than the first as a final reaction to give a vulcanized product. The steps were therefore reversed in making (1) unsaturated polyesters and (2) mixed polymers[6].

Unsaturated polyesters.—A typical polyester with recurring polymerizable groups is polyethylene itaconate:



Polyethylene itaconate was prepared by esterification of equal molar proportions of ethylene glycol and itaconic acid. This polyethylene itaconate was a viscous sirup which did not polymerize readily in bulk, even in the presence of benzoyl peroxide. A thin film, however, hardened in 4 days at room temperature to a

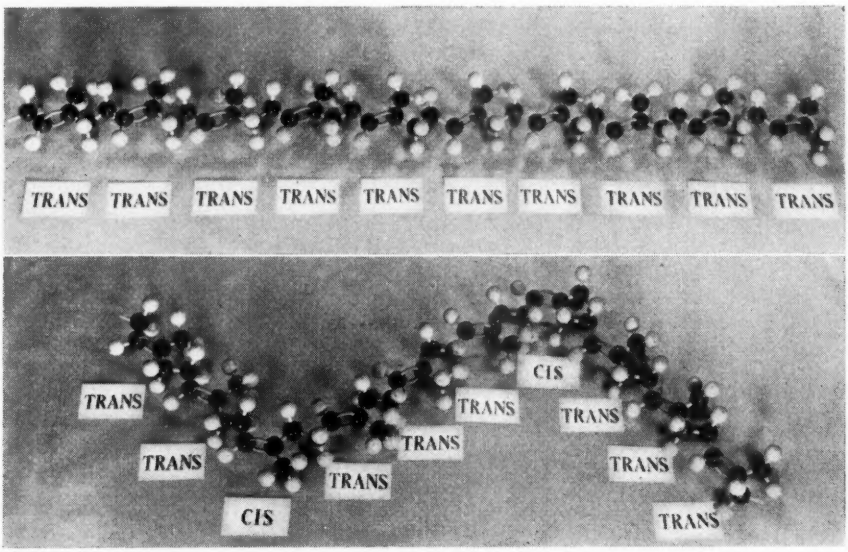
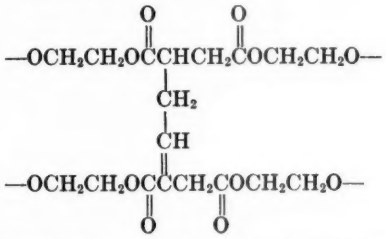


FIG. 1.—Section of rubber molecule with all of the double bonds in the *Trans* position (*above*) and with two of the double bonds converted to the *Cis* arrangement (*below*).

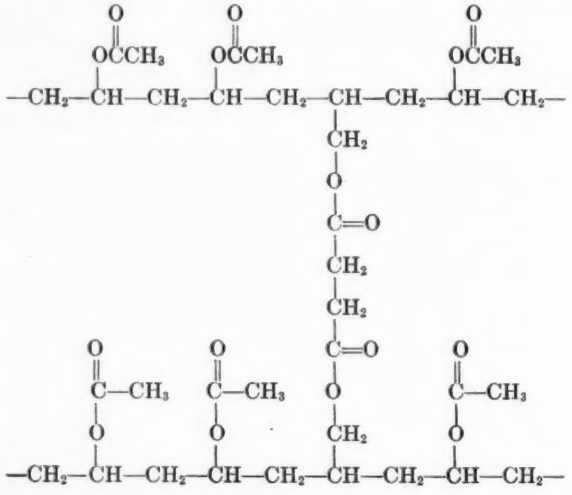
tough, insoluble, abrasion-resistant varnish. The structure of the hardened material was probably as follows:



Polyesters of similar properties were made by the esterification of dibasic acids with the unsaturated glycols obtained by hydrolysis of butadiene dibromide.

Mixed polymers.—If a small proportion of divinyl phthalate be added to vinyl acetate and the mixture polymerized together, the resulting polymer should have essentially the same structure as the product obtained by ester interchange between polyvinyl acetate and diethyl phthalate.

Because vinyl esters were difficult to make in the laboratory, allyl esters, which can be readily prepared by standard procedures, were used instead. When mixtures of vinyl acetate and diallyl succinate containing 1 per cent of benzoyl peroxide were warmed, they polymerized to insoluble nonthermoplastic products. These polymers probably had the following general structure:



The properties of the mixed polymers varied widely, depending on the proportions of diallyl succinate and vinyl acetate. With 0.01 to 0.1 per cent of diallyl succinate, the polymer was not readily soluble but was thermoplastic. It could be milled on a rubber mill and moulded in a press. With 1.0 per cent or more of diallyl succinate, the polymers were no longer soluble or thermoplastic. When heated they became flexible and elastic. On a hot rubber mill they ground to fluffy powders. As the amount of diallyl succinate was increased above 1 per cent, the changes were not so pronounced, but the degree of swelling in solvents decreased and the resistance to temperature changes increased. The products also became somewhat more brittle.

This work establishes rather definitely the fact that thermoplasticity and solubility can be eliminated by means of chemical cross-bonds. At the same time it presents another difficult problem which emphasizes the importance of vulcanization in rubber technology. The unvulcanized materials are mobile, volatile liquids. During polymerization there is a volume decrease of about 20 per cent. Under these conditions it is difficult to make good moulded products.

Better processing characteristics could be obtained by mixing diallyl succinate with previously polymerized vinyl acetate. The idea of mechanical cross-bonds, developed during the study of natural rubber, suggested that diallyl succinate could be used to advantage as a vulcanizable plasticizer for polyvinyl acetate.

Mechanical cross-bonds.—The concept of a purely mechanical type of cross-bond was advanced[4] to explain the possible effect of a *cis-trans* rearrangement during the vulcanization of rubber. Chemical considerations had suggested that this type of rearrangement might be an important factor in vulcanization. Figure 1 shows a section of rubber molecule with all of the double bonds in the *trans* arrangement, and the same molecule with two of the double bonds converted to the *cis* arrangement.

In the first picture the fiber molecule is relatively smooth and straight, in the second it is kinky. A mass of fiber molecules of the first type in random arrangement would be easily distorted by pressure and could be disintegrated by the easy removal of individual fibers through solvent action. It would be plastic and soluble. If the fiber molecules became kinked while in the mass, they would become so badly tangled that the fibers would not slide past each other, the pile would be difficult to distort, and individual fibers could not be pulled from the mass easily. It would be nonplastic and insoluble. The mechanical entanglement of the kinked fibers would hold parts of the different fibers in fixed positions relative to one another in much the same manner that straight fibers would be held if they fused together at the points of contact. This type of mechanical entanglement is referred to as mechanical cross-bonds.

Vulcanizable plasticizers.—The concept of mechanical cross-bonding suggested that, if diallyl succinate were polymerized in the presence of polyvinyl acetate, the highly branched and cross-linked polymer of diallyl succinate would be so tangled with fiber molecules of polyvinyl acetate that the latter would be vulcanized by mechanical bonds. Furthermore, the diallyl succinate should plasticize the polyvinyl acetate so that before vulcanization it would be soft and plastic. This proved to be the case, and therefore diallyl succinate was called a "vulcanizable plasticizer"[5].

Polyvinyl acetate is a hard thermoplastic resin. With one third its weight of diallyl succinate it gave a soft plastic mixture which was completely soluble in acetone and could be milled on a rubber mill. This mixture corresponded roughly to milled crude rubber. Benzoyl peroxide was added on the mill and the mixture cured in a press at 250° F. The product was no longer thermoplastic and was almost insoluble in acetone. When heated it was flexible and elastic. This product corresponded roughly to vulcanized rubber.

The decrease in plasticity during curing depends on the amount of vulcanizable plasticizer used. With increasing amounts of plasticizer, the decrease becomes correspondingly greater. Before heating, the softness of the mixture increases with the amount of plasticizer until it becomes liquid. After heating, the products with more vulcanizable plasticizer are less thermoplastic than those with smaller amounts.

The effectiveness of the vulcanizable plasticizer also depends on the molecular weight of the polymer used. Quantitatively this is best shown by the effect on solubility. Four polymers of vinyl acetate having relative viscosities of 2.5, 7.0, 15.0, and 30.0 were mixed in the following recipe and cured in a press for one hour at 250° F:

Polyvinyl acetate	30 grams	or 71.4 per cent
Diallyl succinate	10 grams	or 23.8 per cent
Benzoyl peroxide	2 grams	or 4.8 per cent

Samples were cut into small pieces and acetone-extracted for 48 hours. The original polyvinyl acetates and the unvulcanized mixtures were all completely soluble in acetone. The acetone extracts on the cured samples compared to the viscosity of the polyvinyl acetates were:

Viscosity of polyvinyl acetate	Acetone extract of cured mixture (percentage)
3.5	62
7.0	28
15.0	13
30.0	12

Comparison of mixed polymers and vulcanizable plasticizers.—These two types of material both require the use of compounds with two polymerizable groups. In mixed polymers, less than 10 per cent of these compounds is needed to give highly vulcanized products. When used as vulcanizable plasticizers, about 25 per cent of the special compound is needed. On the other hand, the plastic masses obtained with vulcanizable plasticizers are more easily adapted to industrial processing operations than are the mixtures of volatile liquids used to make mixed polymers.

The compounds containing two polymerizable groups have the generalized structure:

$$H_2C{=}CR{-}(A){-}CR'{=}CH_2$$

for which the essential characteristics may be satisfied by a variety of chemical types. For example, the (A) component may be an ester, an ether, a ketone, or a hydrocarbon, and its mass may likewise be varied. Control of these two variables, structure and mass, permits wide variation in the chemical and physical characteristics of the vulcanized products obtained.

THEORETICAL DISCUSSION

The results of this investigation have a significant bearing on the theory of vulcanization, on the theory of rubber structure, and on the general relation between the physical properties and constitution of polymeric materials.

Elasticity.—From the description of the properties of a rubber compound before and after vulcanization, given at the start of this paper, it is apparent that vulcanization has (1) decreased the plasticity in the most favorable temperature range for elasticity, (2) raised the upper temperature limit of elasticity by decreasing flow at high temperatures, and (3) lowered the lower temperature limit of elasticity by decreasing the hardening at low temperatures.

The composition and properties of the products described above indicate that either chemical or mechanical cross-bonds lower the plasticity and raise the upper temperature limit of elasticity. They do not lower the lower temperature limit of elasticity; in fact, they seem to raise it somewhat. The lowering of the temperature range of elasticity by vulcanization must be due to some other type of reaction. This reaction is probably of a type which would lower the melting point of simpler molecular species. The basis for such a statement is that, when heated, hard products which contain chemical cross-bonds become elastic instead of melting as do corresponding hard products without chemical cross-bonds. In a somewhat similar manner the addition of liquids to products without cross-bonds produces fluid or semifluid mixtures, but where cross-bonds exist the mixtures are elastic. In either case the hard product with cross-bonds is made elastic by the presence of a fluid component. This, of course, is just another way of saying that elastic recovery is due in large measure to the thermal motion of atoms. Treatments of this entropy effect are available in the work of Karrer[10], Mark[12], Guth[8], Busse[1], and others.

Solubility.—It seems obvious from the results given above that either chemical or mechanical cross-bonds can reduce or eliminate the solubility of an otherwise soluble material.

Tack.—It is not apparent how the tack of unvulcanized rubber is eliminated by vulcanization. In fact, there seems to be no theoretical treatment of this peculiar characteristic of rubber in spite of its great technical importance. A

study of this property might throw considerable light on the structure of rubber and the nature of vulcanization.

Tensile strength.—The tensile strength of rubber is high only after vulcanization, and depends to a considerable extent on the technique used in obtaining the vulcanizate. For example, it is possible[7] to modify widely the tensile strength and brittleness of rubber by small changes in the amount of sulfur (1-5 parts on 100 parts of rubber) by changing the accelerator, by the addition of zinc oxide, or by a small change in the time of vulcanization. These facts suggest that the nature of the vulcanization reaction has an important influence on the tensile strength obtained. The idea that the ultimate tensile strength of the vulcanizate depends on the chain length of the rubber molecules is supported by the fact that excessive breakdown of rubber on a mill results in lower tensile strength when other conditions are constant.

The properties of the products described above indicate that the formation of a large number of chemical cross-bonds results in a weak brittle product. This may be due to a rigidity of this type of bond which does not permit stress distribution. Mechanical cross-bonds, being less rigid, may permit wider stress distribution and result in tougher stronger products. On the other hand, mechanical cross-bonds, as obtained with vulcanizable plasticizers, are less effective than the chemical cross-bonds in the mixed polymers in suppressing plastic flow and solubility. As a result, the number of mechanical cross-bonds required for a good vulcanizate is much higher than the number of chemical cross-bonds.

The variation in the properties of the polymers of vinyl acetate, methyl methacrylate, styrene, etc., with increasing molecular weight suggests that there is a minimum chain length which is necessary for good tensile strength. This minimum is probably at least 1000 carbon atoms.

It may be that the structural basis for a well vulcanized product of high tensile strength is a combination of adequate chain length, a large number of mechanical cross-bonds (considerable entanglement) depending on the shape of the molecular chains, and a small number of chemical cross-bonds. It is probable, at least, that such a structure would have the desired characteristics.

Vulcanizing reactions.—This work has emphasized that the vulcanization reaction itself must meet certain requirements to be useful in the production of thick moulded pieces. Any reaction which releases volatile products is undesirable because of the difficulty of removing the gases from the interior of the product. An equilibrium reaction, such as esterification, where the accumulation of products formed tends to stop the vulcanizing reaction is not satisfactory because of the difficulty in producing the desired physical properties. The most suitable reactions would seem to be isomerization and direct addition, including addition polymerization.

COMMERCIAL POSSIBILITIES

A number of the materials prepared in the course of this study seem to offer attractive possibilities for commercial development, especially in the paint and plastics industries.

Unsaturated polyesters.—The liquid esters made from succinic acid and the butene diols or from ethylene glycol and itaconic acid are types of polyesters which seem adaptable as drying oils, and which suggest interesting possibilities in this important field.

Mixed polymers.—The mixed polymerization of compounds containing one polymerizable group with those containing two polymerizable groups makes

possible the modification of many common polymers in such a manner as to improve their usefulness. For example, vinyl acetate and diallyl succinate can be polymerized together to give a series of products, some of which are slightly less plastic than polyvinyl acetate, and some of which are entirely insoluble and nonthermoplastic. These products should be useful for improved types of polyvinyl acetate and for new types of cast plastics.

Vulcanizable plasticizers.—Vulcanizable plasticizers have been used to treat many high-molecular and resinous materials. In every case the change was similar to that produced by these materials with polyvinyl acetate. Among the materials so treated were polyvinyl chloride, polystyrene, polymethyl methacrylate, cellulose acetate, shellac, asphalt, Arochlor, Halowax, and ester gum.

The properties of both the cured and the uncured products can be varied by the ratio of vulcanizable plasticizer, by the nature of the vulcanizable plasticizer, by the solid used, and by modifying ingredients such as normal plasticizers and pigments. If the unvulcanized material is a plastic solid it can be used as a moulding plastic. If it is liquid, either at room temperature or when hot, it can be used as a cast plastic. The liquid mixtures and solutions of the solid ones can be used as paint and varnish materials.

The possibility of obtaining vulcanized moulded articles from polyvinyl acetate, acrylic esters, cellulose derivatives, and shellac should extend the range of usefulness of these materials.

The free flow of Halowax, Arochlor, etc., can be largely suppressed by the use of selected vulcanizable plasticizers, and such mixtures should furnish fireproof insulating materials for insulating armature coils, tape, paper, etc. The flow of soft asphalt can be suppressed so that softer and less brittle asphalts can be used where hot flow would otherwise eliminate them.

A number of these systems show potential value as paints and baking enamels. The physical and chemical properties of the films can be varied over a wide range by selection of the polymer, plasticizer, and the ratio of the two. Chemically some of these are esters, as are the usual drying oils. Others, however, are entirely different in chemical nature, and it is possible to make a hardened film from hydrocarbons.

The use of a vulcanizable plasticizer with a wide range of materials improves their workability before, and decreases solubility and thermoplasticity after vulcanization. Such products are useful as impregnating materials, moulded plastics, and paint bases.

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VULCANIZATION OF RUBBER BY NITROGEN COMPOUNDS *

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The active influence of nitrogen compounds on the structure of the sols of bivinyl polymers, with consequent colloidization of the system, would lead one to assume that films obtained by evaporation of the treated sols would have better mechanical properties and greater elasticity than films of the unmodified polymers.

The considerable activity of nitrogen compounds in rubber was first observed by Buizov[1], who directed attention to the vulcanizing action of diazoaminobenzene.

Ostromislensky[2] pointed out that nitrogen compounds are capable of producing phenomena in rubber similar to normal vulcanization with sulfur.

Alessandri carried out a reaction of rubber with nitrosobenzene, which was later similarly studied by Bruni and Geiger, and by Pummerer and Gündel.

In 1937 Levi[3] observed the transformation of rubber which is brought about by brief heating with diazo compounds and leads to a condition outwardly resembling vulcanized rubber. Levi called particular attention to the fact that the most active agent, diazoaminobenzene, when heated to 150° C, produces free nitrogen amounting to two-thirds of the entire quantity of nitrogen, with the formation of *o*- and *p*-aminobiphenyl.

Levi drew the conclusion that diazoamino compounds are vulcanizing agents only if they decompose, with evolution of nitrogen, at a temperature near the point of vulcanization, and also contain in their molecules one nitrogen atom united directly to the diazo group.

Further, Levi studied nitrogen compounds (azobenzene and azoamino compounds, *p*-aminoazobenzene) and found them completely lacking in vulcanizing power, for not a single one of these compounds has a free diazo group.

In our previous studies[4], it was pointed out that introducing bivinyl polymeric substances into the sol with nitrogen compounds of the polar group (chryzoidine, benzidine, nitrosodimethylaniline, etc.) causes the development of a micellar structure. As a consequence, a critical displacement ($\theta > 0$) results, that is, elasticity is created, and is revealed by an abnormal viscosity and deviation from the Poiseuille law.

Among the polar nitrogen compounds which the present authors studied were *p*-nitrosodimethylaniline, diazoaminobenzene, *m*-dinitrobenzene, dianisidine, diphenylamine, ammonium oleate, and azobenzene. To explain the relative chemical effects, the action of *p*-quinone also was studied. The compounds were placed in a 4 per cent toluene sol polymer, sealed up in capsules and heated at 110°, 130°, and 160° C for different times.

The mechanical properties of the polymer films were judged by the speed of their plastic flow under constant load[5].

EXPERIMENTAL PROCEDURE

The specimens obtained were tested for their plastic flow in a special apparatus consisting, on the one hand, of a horizontal sheet or plate provided with a catch,

* Translated by Lewis Bertrand from the *Colloid Journal* (*Journal of Theoretical and Applied Colloid Chemistry and Physics*), Vol. 6, No. 2, Pages 175-182, 1940.

and, on the other, a throw-over pulley. Along the sheet moved a small specially constructed aluminum carriage, to produce only slight friction, on one side of which was a catch, on the other a hook. The film specimen was held fast between the two catches on sheet and carriage, following which a load attached to the carriage was dropped over the pulley, causing the carriage to move across the scale, and thereby stretching the film. The stretch of the film was recorded at fixed intervals of time on the scale with which the sheet was provided.

In these experiments the process of plastic flow of rubber was studied, that is, its changes in elongation from the time it was placed under constant load. The volume of the specimen was assumed to be constant during stretching, since the Poisson coefficient amounted to 0.5. Consequently the change in cross-section of the specimen can be regarded as a magnitude which stands in simple ratio to the change in length, and can be calculated from the initial dimensions of the specimen and the amount of stretch, as follows:

If the original length of the specimen is l_0, the alteration in length is Δl, the original cross-section or profile is S_0, and the corresponding increase in length is $\Delta l/S$, we may then, assuming constant volumes, set down the following equations:

$$S_0 l_0 = S\,(l_0 + \Delta l)$$

$$S = \frac{S_0}{l+E},$$

where

$$E = \frac{\Delta l}{l_0}$$

The actual strain or tension for the particular section figured by us for each point of the curve was derived by the formula:

$$P = \frac{F}{S} = \frac{F}{S_0}\,(l+E)$$

From the data obtained, curves of the plastic flow were constructed, that is, the relations between the percentage elongation (ordinate) and the time in minutes (abscissa) for all the films modified by the polar ingredients, according to the duration and temperature of the heat treatment and the concentration of the polar ingredients.

The tests demonstrate beyond a doubt that adding polar compounds to the polymer, followed by heat treatment, produces a more or less substantial degree of stability of the films.

For the unmodified polymer, heat treatment leads to a reduction in the time of rupture of the film specimen and an increase in the relative elongation (Figure 1). Introducing more active modifiers, *e.g.*, *p*-nitrosodimethylaniline and diazoaminobenzene, increases the elastic qualities of the films, converting plastic flow into elastic extensibility. Whereas a film of the normal polymer breaks within a single minute, the same film, as a result of the action of *p*-nitrosodimethylaniline, does not break for 2 to 6 hours (Figure 2).

The compounds tested had the effects described only under conditions of preliminary heat treatment of the sol, without which the stability of the films is not increased[6].

By adding diazoaminobenzene to the sol a structural development is again observed, although to a lesser extent than with *p*-nitrosodimethylaniline (Figure 3).

The heat treatment of the toluene sol (4 per cent) polymer, containing diazoaminobenzene in the absence of oxygen, considerably augments the activity of the added ingredient, causing the sol to become a gel.

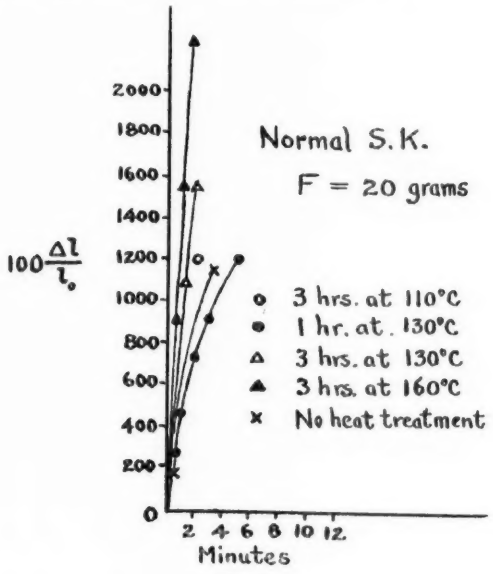


FIG. 1.

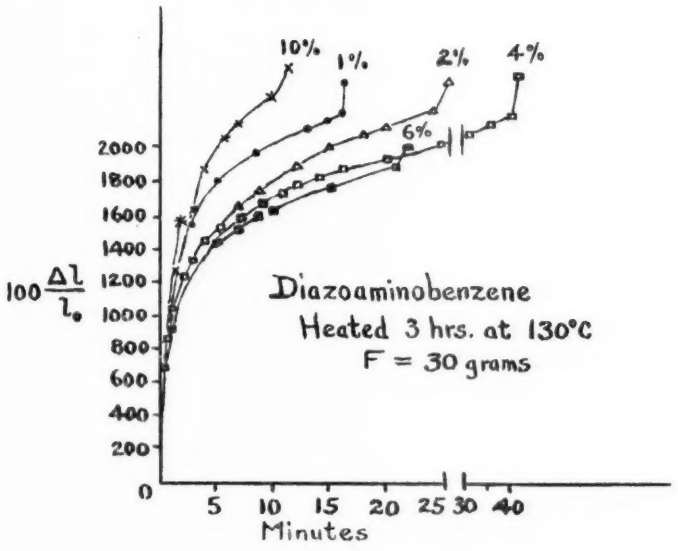


FIG. 2.

Diphenylamine was used to ascertain the effect of a substituted amino group. As was to be expected, in the present instance only a negligible structural development was observed, which can be ascribed to the absence in the molecule

of biphenyl of the active group for rubber. Addition of dianisidine and azobenzene to the toluene sol of the polymer is likewise practically without effect on the development of the colloidal structure. The stability of the films obtained from such sol differs slightly from that of films of unmodified rubber.

Ammonium oleate was selected by us as a substance containing pentavalent nitrogen. As has been previously demonstrated, pentavalent nitrogen is not active in the sense that it affects the structural formation of rubber. The data obtained with the films confirmed this.

Figure 4 shows the relation between the intensity of the modifying action and the concentration of the added ingredient. In this case we have the repeatedly-observed characteristic relationship for the active added ingredient, with a sharply defined maximum effect of concentration. For most compounds such a maximum is found within the range of 2 to 4 per cent of added ingredient, based on the polymer.

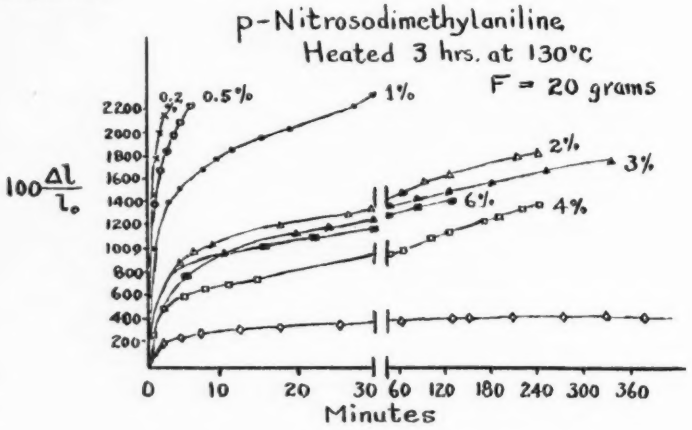
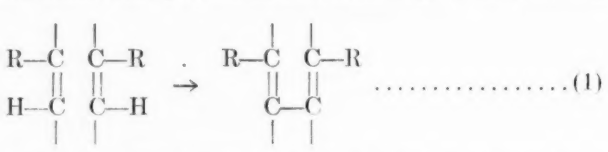


FIG. 3.

From the viewpoint of organic chemistry, we may assume that the effects observed are conditioned by the oxidation reactions of the rubber on account of the nitroso group, with subsequent polymerization, according to the following scheme.



.....(1)

To explain the significance of these chemical effects, the action of *p*-quinone was studied at the same time as that of the nitrogen compounds. *p*-Quinone is a strong oxidizing agent, and readily combines with two atoms of hydrogen to form hydroquinone, thus:

$$2H + C_6H_4O_2 \rightarrow C_6H_4(OH)_2$$

At the same time, quinhydrone, distinguished by its deep green color, was formed as an intermediate product.

In the polymer the following phenomena take place. The effects of quinhydrone are clearly visible under the microscope and, consequently, if any chemical

reaction were of significance here, corresponding to scheme (1), a considerably greater modifying effect than in the presence of nitrogen compounds would have been found. Yet, although the effect of *p*-quinone is to render the films more stable (Figure 5) but less than *p*-nitrosodimethylaniline and diazoaminobenzene, it may be concluded that the oxidation reaction in this instance does not play a decisive part.

For the particular compounds which were examined, the following conclusions can be drawn.

The addition of nitrogen compounds may cause the development of a colloidal structure, leading to increased elastic qualities in the polymer, and transformation

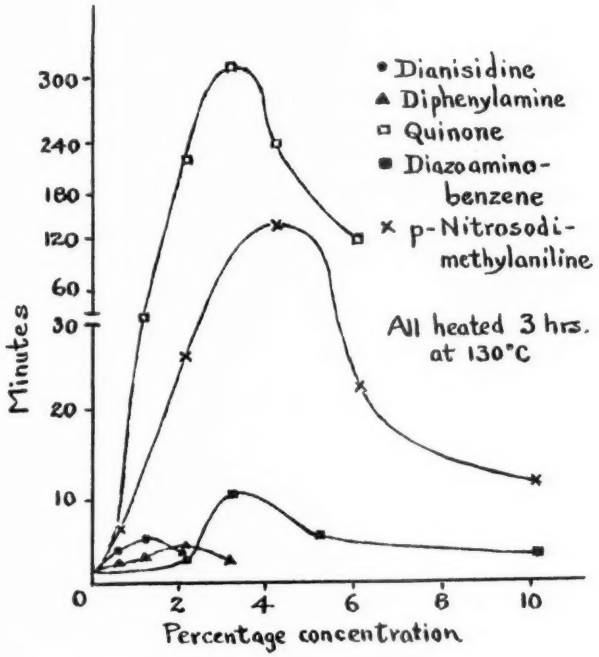


FIG. 4.

of plastic flow in the film into elastic extensibility. At the same time, the mechanical stability of the films is increased. The ingredients which were tested showed the following relative activities:

p-nitrosodimethylaniline > diazoaminobenzene > *p*-quinone > dianizidine > diphenylamine > azobenzene.

Their activity increased with increase in the dipole moment, that is, with increased asymmetry in the distribution of the polar group in the molecule. *p*-Nitrosodimethylaniline and diazoaminobenzene were found to have especially strong effects. The addition of polar substances produced considerable activity only after preliminary heating treatment in the sols.

The optimum conditions of heat treatment, for the most active of the added ingredients, was approximately 3 hours at 130° C. Heat treatment in the absence

of oxygen did not affect the results in any essential respect. Thus, oxygen is not necessarily a participant in the action of the added ingredient. The addition of *p*-quinone had considerably less effect than the addition of polar nitrogen compounds. With oxygen present during the heat treatment, the activity of *p*-quinone was greater. In the case of diazoaminobenzene, heat treatment of the toluene sol in the absence of oxygen (in nitrogen) increased considerably the effect of the ingredient, causing cooling, which did not occur with treatment in air.

The relation between the mechanical properties of films and the concentration of active ingredients (for example, during the time of flow of the film until its rupture under an equivalent initial stress or critical elongation) is expressed for all the polar substances by curves with sharply defined maxima lying between 2 and 4 per cent of the substance added (based on the crude rubber). The

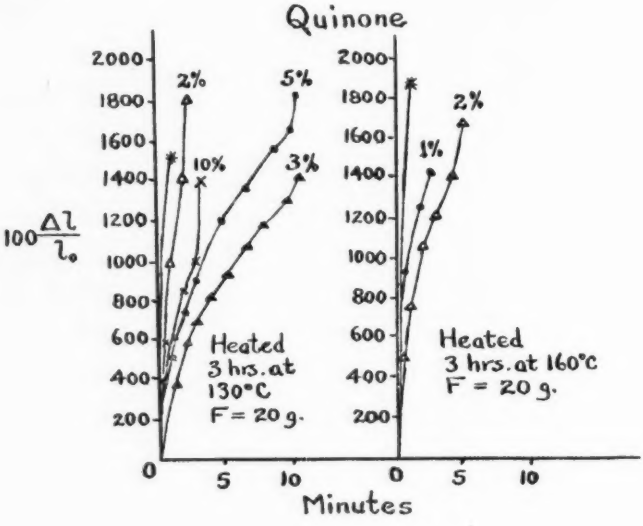


FIG. 5.

optimum concentration of the added ingredient, corresponding to the maximum increase in the mechanical properties, evidently corresponds to the greatest chemico-adsorptive activity.

The critical point of displacement in 2 per cent sol of the sodium bivinylene polymer by the action of the active ingredients increased from 0 to 14-24 dynes per sq. cm., while such a maximum increase in structure corresponds to 2 per cent of reagent added, and the curve showing the relation between the concentration of the ingredient added, and the resulting activity has the same general shape as for the mechanical properties of the films.

Heat treatment of the more concentrated (8 per cent) sol of the polymer in toluene with diazoaminobenzene causes cooling and the formation of a stable cooling lyogel, with a decidedly sharp increase in the critical displacement stress from 55 to 2600 dynes per sq. cm. for the optimum effect of the added ingredient. The control heat treatment of the sol in the absence of an active material does not cause cooling and yields $\theta = 65$ dynes per sq. cm. Under these circumstances

the relation between the critical displacement stress and the concentration of diazoaminobenzene was found to be analogous to the relation previously found (for the sol and the film), but with the maximum closer to the higher concentrations of added material (approximately 6 per cent).

The mechanism of the action of nitrogen compounds may be considered as the formation of structure-forming centers as a result of combination of a molecule of active ingredient with the polar groups. The hydrocarbon portions of such centers tend toward the outside and combine with the low-aggregate fractions of the rubber, thereby increasing their degree of aggregation. In addition, the polar molecules form peculiar bridge-like viaducts connecting the chains of the polymer in the micelles.

A study of the action of sulfur and of thiuram dissolved in toluene sols of the polymer showed that, by heat treatment similar to that carried out in the tests with nitrogen compounds, improvements in the mechanical properties of the films and sols (cooling) were obtained, such as described above (in the investigation of the films, heat treatment of the products containing sulfur and thiuram as well as diazoaminobenzene and nitrosodimethylaniline, added for comparison, was used with the films).

The results indicate that vulcanization of rubber is a complicated chemico-adsorption process, which leads to a highly developed colloidal structure as a result of displacement of the fractional equilibrium and colloidization of the low-aggregate fractions of the crude rubber.

The authors wish to express their thanks to Prof. P. A. Rebinder for his helpful guidance and assistance in this work.

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DYNAMIC PROPERTIES OF RUBBER

DEPENDENCE ON PIGMENT LOADING *

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Dynamic tests for rubber compounds become pertinent wherever the rubber in use is subjected to repeated deformations, especially if these deformations are frequent enough and large enough to cause the generation of appreciable quantities of heat. These conditions exist in such a large number of important applications of rubber that it is not surprising to find tests being evolved to measure compounds under dynamic conditions. Representative of this trend is the work of Kosten[5-8], Roelig[13], Naunton and Waring[10, 11], and Yerzley[15, 16]. These authors have described tests which differ widely in character, but are designed to determine the dynamic modulus of rubber compounds and to give a means of estimating the energy dissipated as heat during repeated deformation.

APPARATUS AND PROCEDURE

A general description of the apparatus and procedure was included in a paper by Sebrell and Dinsmore[14]. Figure 1 is a photograph of the equipment.

The driving system utilizes a principle which is old for the fatigue testing of metal and has been used more recently by Naunton and Waring [10] for rubber. It consists of a rebuilt loud-speaker unit with a field coil which provides a saturated magnetic field of about 7500 gauss in the air gap. The coil which vibrates in this field consists of two layers of No. 25 enameled copper wire, each layer containing about twenty turns. The diameter of the coil is 2 inches (5 cm.). The coil was formed by winding the wire on a core covered with a layer of paper impregnated with Bakelite varnish. The coil was then painted with the varnish, dried, and baked.

The vibrating coil is attached by small screws to a brass cone, along the axis of which passes a threaded brass rod. This assembly is shown in Figure 2. The rod passes through a clearing hole in the center post of the speaker and projects at the bottom of the speaker (Figure 3). A set of cantilever centering springs is attached at the brass cone and at each end of the rod. Each set consists of two thin steel blades at an angle of 90° to each other and lying in a plane perpendicular to the brass rod. Screw adjustments are provided at the ends of the springs to center the rod.

The central rod transmits the vibratory force to the middle plate of the system of yokes, shown in Figures 1 and 3. Two rubber test-pieces are used, one on each side of the middle plate. These test-pieces are centered with the help of shallow recesses in the plates. The bottoms of the recesses are covered with very fine sandpaper. In this work the test-pieces were moulded cylinders, 0.5 inch (1.27 cm.) high and 0.75 inch (1.9 cm.) in diameter.

The static compression of the test-pieces is exactly determined by introducing the test-pieces in the following way: with the middle yoke loose on the rod the test-pieces are put in place, and the hand screw at the left-hand end of the

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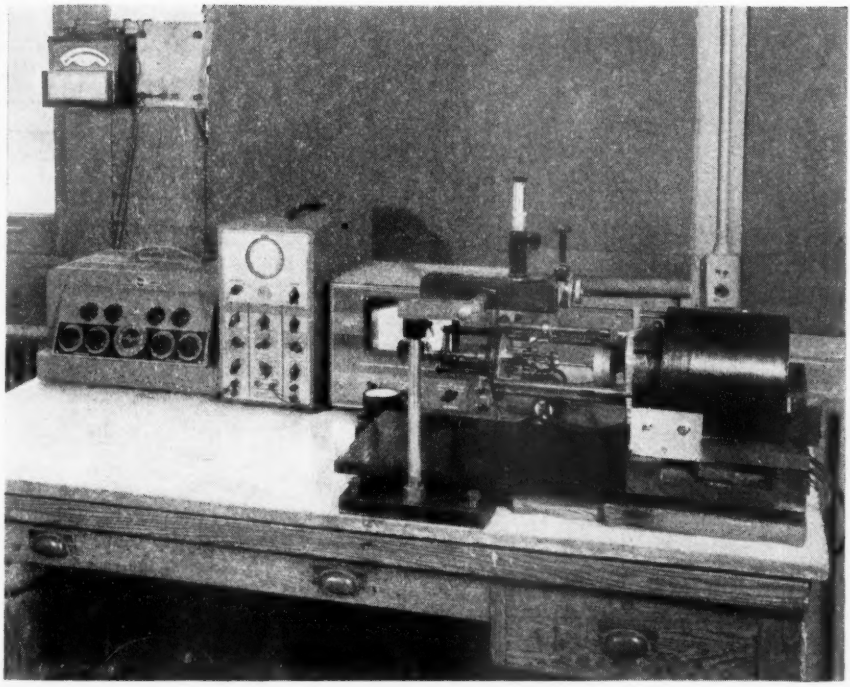


FIG. 1.—Photograph of equipment.

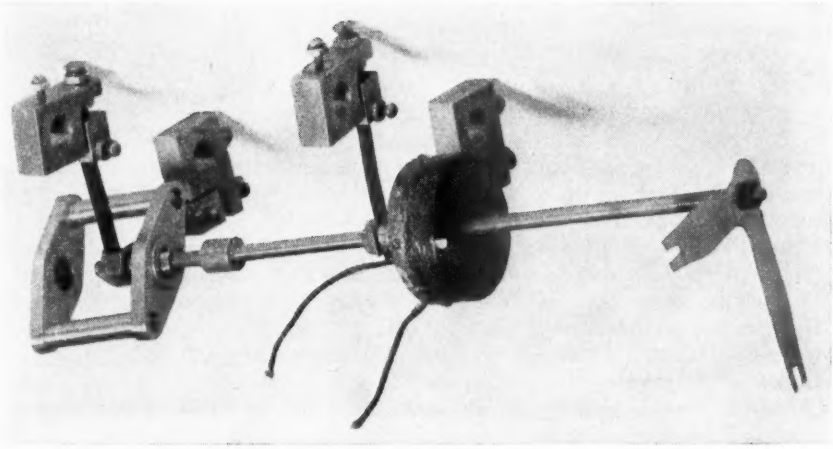


FIG. 2.—Vibrating coil and spring assembly.

apparatus is turned against a plunger which passes through the top plate. This advances the plunger through the top plate until a shoulder on the plunger comes into contact with an accurately machined spacer. The middle yoke is then fastened in position on the threaded rod by means of nuts. In this work the compression was invariably 8 per cent.

To increase the mass of the speaker unit, it is set in a heavy cylindrical shell weighing about 75 pounds (34 kg.). This is evident in Figures 1 and 3. The entire system is mounted on Airfoam cushions so that it is effectively isolated and no appreciable energy is transmitted to the table.

Power at 60 cycles per second can be supplied to the vibrating coil conveniently by a variable transformer. But tuning of the system to resonance is facilitated by the use of a power supply of variable frequency, even though the measure-

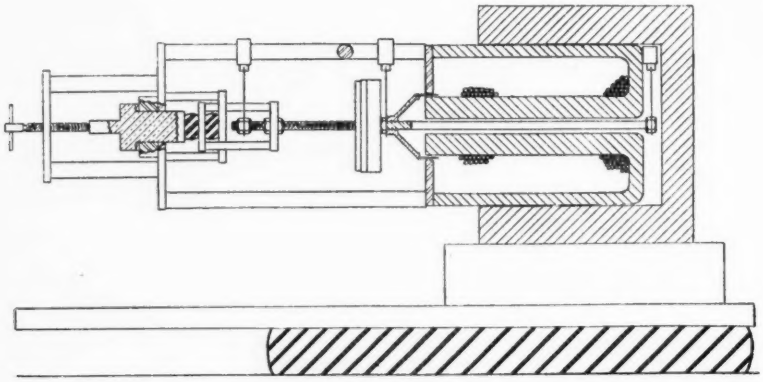


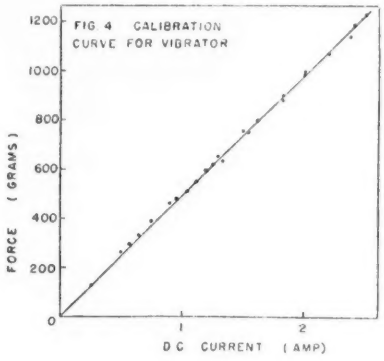
FIG. 3.—Drawing of vibrator.

ments are all made at 60 cycles. For this reason a Jackson resistance tuned audio oscillator is used in conjunction with a Lafayette 100-watt amplifier to energize the vibrating coil. An R.C.A. cathode ray oscillograph, synchronized with the 60-cycle line, serves to check the frequency and the wave form.

In carrying out a determination of dynamic properties, the test-pieces are put in place and, on the basis of experience, weights are added to the vibrating system to approximate resonance. The weights are slotted to slip on the central threaded rod, and are held in place by tightening two knurled disks against them. This arrangement is shown in Figures 1 and 3. Power is supplied to the vibrating coil and the frequency is varied to locate the resonance point, which is the frequency for maximum amplitude as observed in the microscope. If this frequency is lower than 60 cycles, determined from the scale of the audio oscillator, weight is removed; if it is higher than 60 cycles, weight is added. By a repetition of this process, the system is tuned to exactly 60 cycles, judged by a stationary pattern on the oscilloscope. In practice, this tuning process is rapid, convenient, and precise. The amplitude at resonance is measured with the traveling microscope (Figure 1), which is focused on a piece of illuminated emery cloth cemented to the vibrating system. The mass of the vibrating system at resonance is 365 grams plus any added weights. The driving force at resonance is determined by the current through the coil. This is read on an alternating current meter, and is controlled by the volume control on the audio oscillator.

To determine the static modulus, a direct current is passed through the coil, and the deflection, after any observable plastic flow has ceased, is measured with the microscope. The deflection is doubled by a reversing switch. The electrical hookup is such that the coil can be switched at will from the alternating to the direct current source.

To evaluate the driving force, it is necessary to calibrate the coil. This is done by passing measured direct currents through the coil, with the field on, and observing the force necessary in each case to return the coil to its equilibrium position. This restoring force is determined by attaching a horizontal cord to the central rod, passing the cord over a pulley, and adding sufficient weight to hold the coil in its equilibrium position. The calibration curve is a straight line (Figure 4). The peak value for an alternating current must be used to calculate the driving force from this direct current calibration.



THEORY

Except for certain deviations which will be discussed later, a vibration theory which assumes a damping force proportional to the velocity is useful in explaining the results with rubber vibrations. The equation of motion for such a system, as ordinarily given in textbooks on vibration, is:

$$m\frac{d^2x}{dt^2}+b\frac{dx}{dt}+sx=F\cos pt \qquad (1)$$

where m = vibrating mass (grams)
b = proportionality factor between velocity and frictional force (dynes per cm. per sec.)
s = spring constant of system (dynes per cm.)
F = maximum value of driving force (dynes)
p = angular frequency (radians per sec.)
t = time (sec.)
x = displacement from equilibrium position (cm.)

In the case of rubber, it is advantageous to consider b and s in relation to the size and the shape of the test-piece. The modulus of elasticity for rubber in compression depends on the shape of the test-piece, unless lubricated end plates are used, which here is not the case[4]. It is possible, however, to replace s and b by values which will be independent of the size of the test-piece, provided the shape is the same.

Young's modulus, as customarily defined, is related to s by the equation:

$$E = s(h/A) \tag{2}$$

where E = dynamic modulus
h = height of test-piece
A = area of end of test-piece

Similarly, b is replaced by a new constant, η, given by:

$$\eta = b(h/A) \tag{3}$$

η is known as the coefficient of normal viscosity[2]. In this text it will be referred to simply as the internal friction. η and E are independent of the size of similarly shaped test-pieces, both according to theory and our experimental tests.

In the vibrating system previously described, two test-pieces are used, so a factor 2 must be introduced into the denominator of Equations 2 and 3 in calculating E and η from experimental results. The factor $h/2A$ will henceforth be referred to as the shape constant, and will be designated by the letter q.

The steady-state solution of Equation 1, in these terms, is:

$$x = \frac{Fq \cos(pt-\theta)}{\sqrt{(E-mqp^2)^2+\eta^2p^2}} \tag{4}$$

$$\tan\theta = \eta p/(E-mqp^2) \tag{5}$$

If x is plotted as a function of p or the frequency, the familiar resonance curve is obtained. The amplitude is large when

$$E = mqp^2 \tag{6}$$

For the purposes of this work, this value of p can be considered to give the maximum amplitude. For the value of p determined by Equation 6:

$$X_{res.} = Fp/\eta p \tag{7}$$

where $X_{res.}$ = amplitude of vibration at resonance.

Equations 6 and 7 serve for the determination of E and η, since all the other quantities involved are susceptible to measurement.

If the system under consideration were vibrating freely instead of being driven, the vibrations would be damped. The magnitude of the damping depends on p, η, and E. Kimball[2, 3] discussed the energy relations for damped vibrations. The vibrational energy is proportional to the square of the amplitude. If the system is driven by a periodic force so that a constant amplitude is maintained, energy just equal to that dissipated as heat must be supplied to the system. Thus, the vibrational energy, calculated for successive free vibrations, gives, at least to a first approximation, a measure of the energy dissipated as heat in the forced vibrations.

Solution of Equation 1 for free vibrations (that is, $F=0$) shows that the ratio of the square of the amplitude of a vibration in the train of damped oscillations to that immediately preceding it is $e^{-2\pi p\eta/E}$. If this quantity is multiplied by 100, it represents the percentage dynamic resilience; that is, the percentage of the vibrational energy which persists in the second of two successive free vibrations; hence:

$$R = 100e^{-2\pi p\eta/E} \tag{8}$$

In this work, R is the dynamic resilience. It is the square of the quantity taken as the resilience by Naunton and Waring[10]. It also differs from the quantity called resilience by Yerzley[15]. These differences will be discussed further in connection with the results. The percentage damping is $(100-R)$.

The damping can be used to compute the relative heat generation in different rubber compounds due to cyclic deformations under various circumstances. Naunton and Waring[11] discussed the conditions which exist, depending on whether the comparison is made for the same deformation or the same force. For the same force:

$$H_f \propto \frac{(100-R)F^2}{E} \tag{9}$$

For the same deflection, X:

$$H_x \propto (100-R)EX^2 \tag{10}$$

A high modulus leads to low heat generation if the comparison is made for the same force, and to large heat generation if the comparison is made at the same deflection. In either case the heat generation is proportional to $(100-R)$.

Equations 9 and 10 represent an extension of the results from forced vibrations to various types of deformation, the force concerned being a deflecting force on the rubber rather than a force which sustains the vibrations of a rubber-mass system.

In the case of forced vibrations of constant amplitude, the heat generated per cycle can be calculated directly by evaluating the integral $\int b\ x\ dx$ for a cycle. The result is:

$$H_f = \frac{\pi F^2 bp}{(s-mp^2)^2+b^2p^2} \tag{11}$$

for comparison at the same driving force F, and

$$H_x = \pi bpX^2 \tag{12}$$

for comparison at the same amplitude X.

When the comparison is made at the same amplitude, the heat generation does not depend on the system being at resonance or not. The result from Equation 11, however, depends on the position of the vibration on the resonance curve. Since rubber, when used to isolate vibrations, functions on the low-frequency side of the resonance peak, the terms containing p^2 in the denominator of Equation 11 can be dropped for an approximate result, giving:

$$H_f = \frac{\pi F^2 bp}{s^2} \tag{13}$$

In terms of η and E, Equations 12 and 13 become:

$$H_x = \pi pX^2(\eta/q) \tag{14}$$

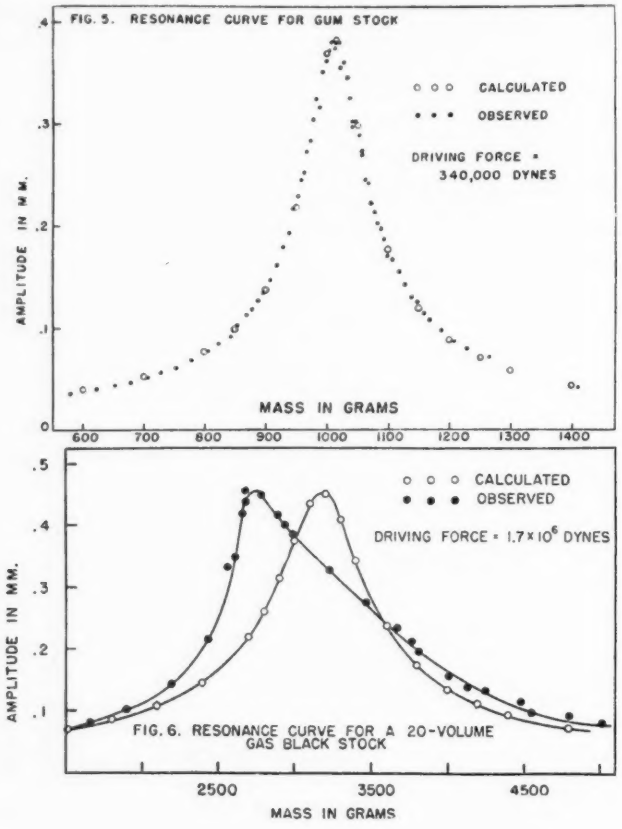
$$H_f = \pi pF^2(\eta q/E^2) \tag{15}$$

The results of relative heat-generating rates for the compounds here studied, calculated by Equations 14 and 15, were very similar to results secured by Equations 9 and 10.

It is known from the work of Kosten[6] and others that η is a function of the frequency. To a first approximation, η is inversely proportional to the frequency.

Some experimental tests of this relation are given in a subsequent section. Here it is advantageous to point out that if the product of η and p is constant, the amplitude at resonance and the resilience will be invariant with frequency. This can be seen from Equations 7 and 8.

As is evident from Equation 4, a system can be tuned to resonance by variation of s, m, or p. In this work, m is varied. This has experimental advantages in that we do not have to depend on the frequency calibration of an electrical



oscillator, and the known variation of η with frequency is thereby eliminated in the comparison of the rubber compounds.

The applicability of the preceding simple vibration theory under the testing conditions can be judged by comparing experimental resonance curves with curves calculated from Equation 4. Figure 5 shows such curves for a gum stock. The calculated curve is made to fit the experimental curve at the resonance peak. No deviation between calculated and observed curves is perceptible.

In the case of rubber compounds containing pigment loadings, there is a dependence of E and η on the amplitude of vibration which is not taken into consideration in Equation 4. This effect will be discussed in more detail in the section dealing with results. It leads to an asymmetrical resonance peak, which

may deviate considerably from that calculated by Equation 4. Such a comparison is shown in Figure 6. If the amplitude of vibration were maintained constant by varying the driving force for different points on the resonance curve, it can be presumed that the agreement of the observed and calculated curves would be greatly improved, since the heat generation would then be the same at all points. Hence, the deviation shown in Figure 6 may not be so much a breakdown of the theory as an indication that the calculated values of E and η apply exactly only for the amplitude of vibration at the resonance peak. This is a vibration characteristic of pigmented rubber compounds which must be taken into account in applying the results of the test. The variation of E and η with amplitude may be associated with warming of the test-piece due to the vibration. Den Hartog[1] discussed the characteristics of vibrating systems for which the stiffness depends on the amplitude. The experimental curve in Figure 6 shows these characteristics to some extent.

COMPOUNDS USED

The stocks used were accelerated with Captax (mercaptobenzothiazole) and were similar in composition, except for the pigment loadings. The cure was 65 minutes at 275° F, unless otherwise stated. The compounds were prepared by the research compounding section of the Goodyear Tire and Rubber Company (Table I).

The blanc fixe series was similar to the Thermatomic black series, with pigment loadings by weight calculated to give volume loadings of 0, 10, 20, 30, 40, and 50 parts.

RESULTS

The results of tests at a frequency of 60 cycles per second are shown by curves. Figure 7 is a plot of the dynamic modulus against the volume loading of the various pigments. Superspectra and channel black have by far the greatest stiffening action of any of the pigments and, in a general way, the curves for all the pigments lie in the order of particle size. This confirms, for vibration, accepted ideas derived from conventional tests of the importance of the area of pigment surface for reinforcement. Figure 8 is a plot of η (internal friction) against volume loading. The curves for the various pigments lie in essentially the same order as the curves in Figure 7. Hence, increased subdivision of the pigment introduces increased internal friction in the stock. This can easily be visualized as connected with the inhomogeneity of structure, shear gradients, and varying conditions of stress distribution around the particles during vibration. Figure 9 shows the effect of a cure variation on the dynamic modulus. As would be expected for this type of stock, the change in cure shown has a rather small effect on the dynamic modulus. No effect on the internal friction due to the increase in cure from 35 to 65 minutes at 275° F could be detected.

The data for Figures 7, 8, and 9 were obtained with a constant driving force of 3.4×10^5 dynes, corresponding to a root-mean-square current of 0.5 ampere through the vibrating coil.

From the curves of Figures 7 and 8, by use of Equations 8, 14, and 15, curves for the dynamic resilience and relative heat generation can be calculated. Figure 10 shows the curves for the dynamic resilience. They are strikingly similar in appearance and relative position to curves published by Parkinson[12], showing the dependence of pendulum rebound values on pigment loadings. The

dynamic resilience is lower, however, than the pendulum rebound. This is due principally to the fact that the rebound indicates the percentage of energy remaining after half a cycle, whereas the dynamic resilience is the energy remaining after a whole cycle[9].

The values for resilience given in Figure 10 are also lower than those reported by other workers on the properties of rubber in vibration. As nearly as can be

TABLE I

SUPERSPECTRA AND CHANNEL BLACK SERIES

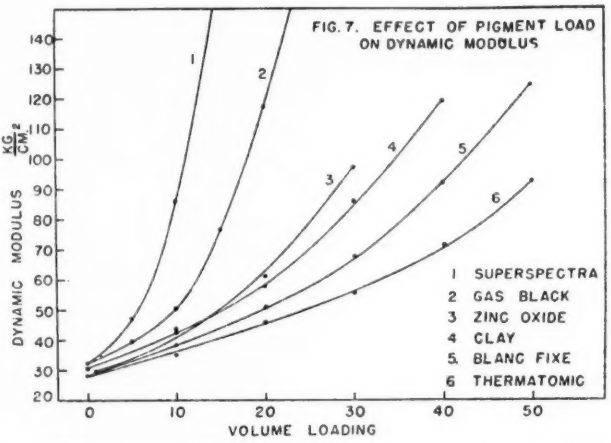
(Parts by Weight)

PIGMENT SERIES								
Smoked sheet	100	100	100	100	100	100	100	100
Zinc oxide	5	5	5	5	5	5	5	5
Sulfur	3	3	3	3	3	3	3	3
Captax	0.5	0.75	0.75	1.0	1.0	1.2	1.2	1.2
Stearic acid	3	3	3	3	3	3	3	3
Phenyl-β-naphthylamine	1	1	1	1	1	1	1	1
Pigment	0	9.5	19	28	37.5	47	56.5	66
THERMATOMIC BLACK SERIES								
Smoked sheet	100	100	100	100	100	100		
Zinc oxide	5	5	5	5	5	5		
Sulfur	3	3	3	3	3	3		
Captax	0.5	0.5	0.5	0.5	0.5	0.5		
Stearic acid	1	1	1	1	1	1		
Phenyl-β-naphthylamine	1	1	1	1	1	1		
Thermatomic black	0	19.9	39.8	59.7	79.6	99.5		
CLAY SERIES								
Smoked sheet	100	100	100	100	100	100		
Zinc oxide	5	5	5	5	5	5		
Sulfur	3.5	3.5	3.5	3.5	3.5	3.5		
Captax	0.5	0.75	0.75	1	1	1.25		
Stearax	3	3	3	3	3	3		
Phenyl-β-naphthylamine	1	1	1	1	1	1		
Clay[a]	0	28	56	84	112	140		
ZINC OXIDE SERIES								
Smoked sheet	100	100	100	100	100	100		
Zinc oxide (XX4)	5	60	120	180	240	300		
Sulfur	3.5	3.5	3.5	4	4	4		
Captax	0.5	0.75	0.75	0.75	0.75	0.75		
Stearic acid	1	1	1	1	1	1		
Phenyl-β-naphthylamine	1	1	1	1	1	1		

[a] Hard Carolina clay pigment.

judged from the data published, this difference does not exist so much in the experimental work as in the varying ways in which the resilience has been calculated. Figure 11 illustrates the amplitude of a damped, free vibration as a function of the time. In essence, the resilience has been defined by various authors in the following ways: Naunton and Waring[10], EF/AB; Yerzley[15], $(EF+CD)/(AB+CD)$; present authors, EF^2/AB^2. It is apparent that Yerzley's value will be the highest, and that of the present authors the lowest of the above ratios. The ratio used by Naunton and Waring corresponds to results with the rebound pendulum, *i.e.*, represents the energy remaining after half a cycle.

The resilience values secured in the vibration test, even if calculated for half a cycle, should not be expected to coincide exactly with those from the pendulum-rebound test. Naunton and Waring[11] give curves showing the percentage rebound of steel balls from rubber blocks for varying sizes of steel balls. The rebound decreases with the size of the ball. Thus, the rebound appears to depend on the experimental conditions. Likewise, as previously noted, the resilience from



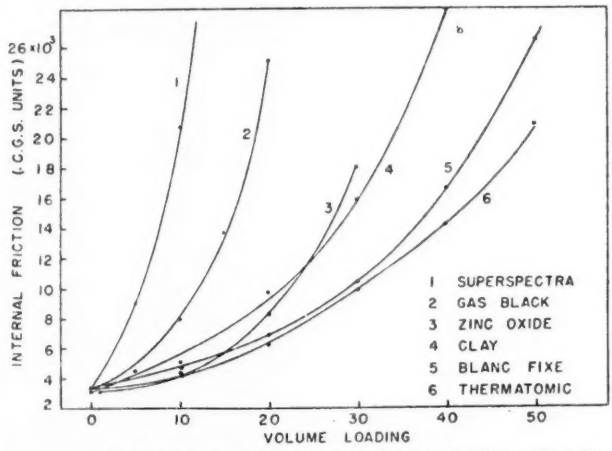
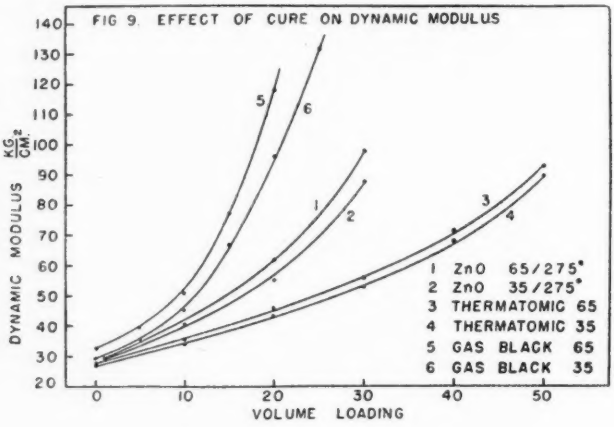


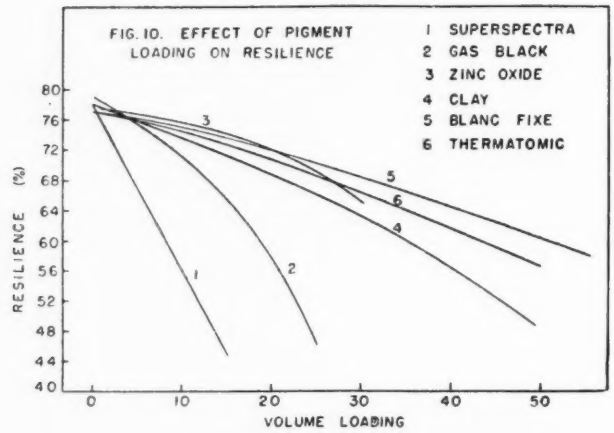
FIG 8. EFFECT OF PIGMENT LOADING ON INTERNAL FRICTION

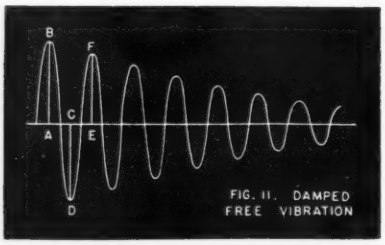
the vibration test depends on the amplitude of vibration and the temperature. These relations must be taken into account in the application of the results.

Figure 12 is a plot of calculated heat generation against the pigment loading, all the compounds being kept in vibration by the same force. Figure 13 shows similar curves for vibration of all the compounds at the same amplitude. The reverse order of the curves in Figure 12, compared to Figure 13, shows how important it is to know to what extent a rubber compound in use is deformed under conditions of constant force or of constant deflection. In a tire, both conditions for deformation probably occur.

Figure 14 is a plot illustrating the dependence of dynamic modulus on the amplitude of vibration. Against the volume loading of pigment is plotted the rate of change of modulus with amplitude. For the range of amplitudes used,







the modulus is essentially a straight-line function of the amplitude. The slope of such lines is plotted as ordinate in Figure 14. The curve for each pigment shows a rather sharp break, the position of which indicates the reinforcement rating

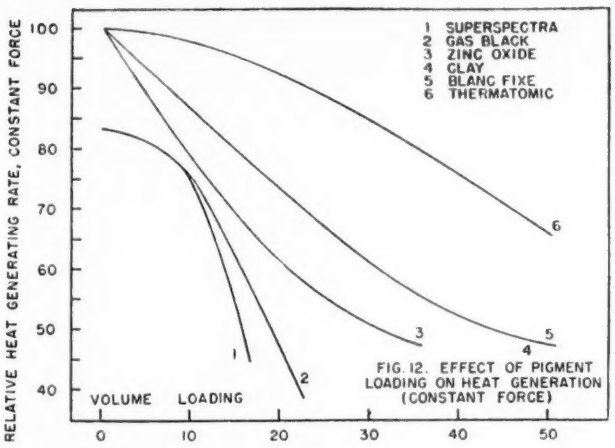
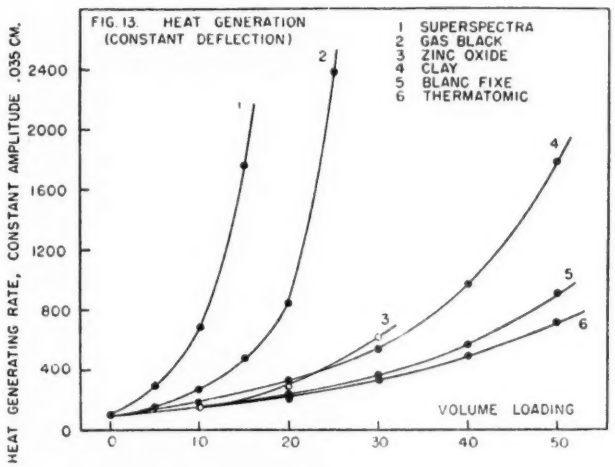
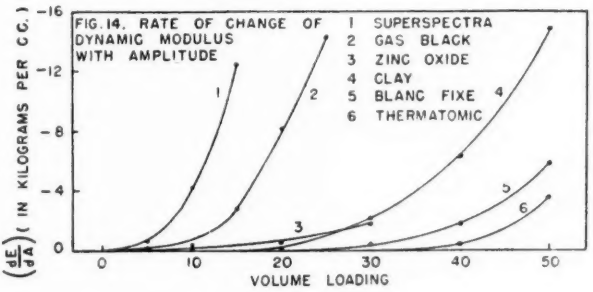


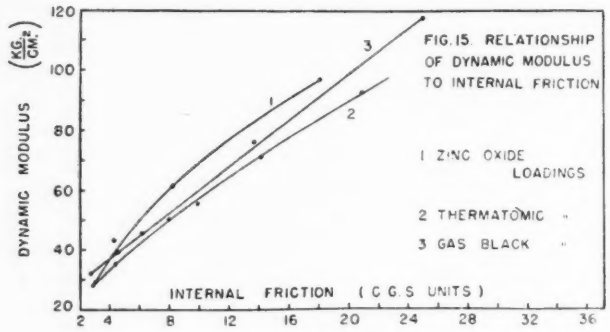
FIG. 12. EFFECT OF PIGMENT LOADING ON HEAT GENERATION (CONSTANT FORCE)





of the pigment. We have been unable to determine whether this dependence of modulus on amplitude is due entirely to warming of the test-piece by the vibration. Since the heat generation increases as the square of the amplitude, this is undoubtedly a factor in the result. The relatively small temperature rise observed in the test, however, throws some doubt on the conclusion that the effect is entirely due to temperature. The dependence of modulus on amplitude was also noted by Naunton and Waring[10].

Figure 15 is a plot showing the approximate linear relation between dynamic modulus and internal friction. The curves are of interest because they indicate that the fundamental mechanism of reinforcement is similar for the different pigments and that stiffening occurs as internal friction is introduced.



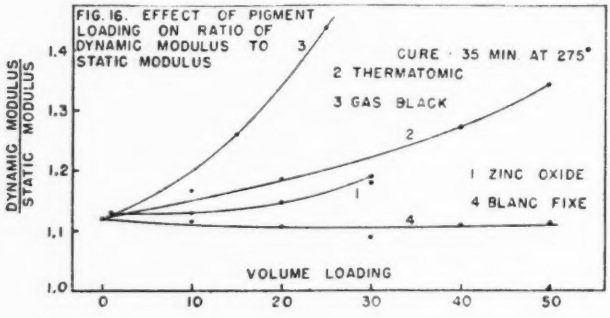


Figure 16 is a plot of the ratio of the dynamic to the static modulus against pigment loading. The curves show marked differences between the pigments. The relative position of the curves is different from that in any of the preceding plots. For channel black, the ratio of dynamic to static modulus is very sensitive to the loading; for blanc fixe it is practically independent of the loading.

In addition to the preceding results at a frequency of 60 cycles per second, some data were secured in a frequency range from 20 to 150 cycles per second. It was found that the dynamic modulus was independent of the frequency in this range. The results are shown in Figure 17. The question arises as to how low the frequency would have to go before the dynamic modulus began to decrease and approach the static value. The amplitude should be taken into account when this question is posed. The dependence of the dynamic modulus on ampli-

tude has already been shown, and at any frequency the dynamic modulus converges toward the static value as the amplitude is increased.

The internal friction is a hyperbolic function of the frequency (Figure 18). As a test of the hyperbolic relation, $1/\eta$ is plotted against the frequency in Figure 19. Here the relation is almost linear, but the slight curvature which exists is sufficient to cause a decrease in resilience with increasing frequency (Figure 20).

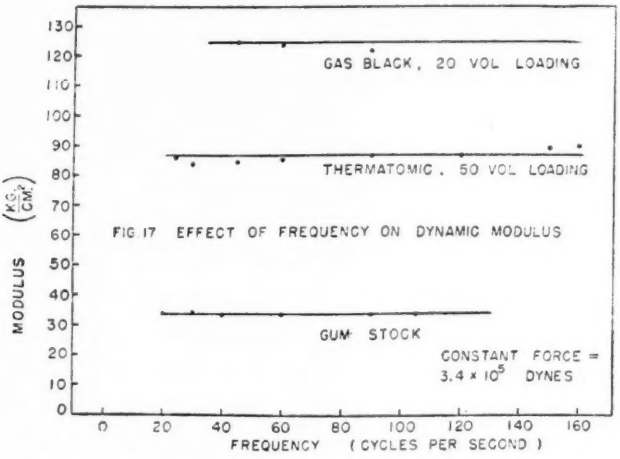

GAS BLACK, 20 VOL LOADING
THERMATOMIC, 50 VOL LOADING
GUM STOCK
CONSTANT FORCE = 3.4 x 10^5 DYNES
MODULUS (KG./CM.^2)
FREQUENCY (CYCLES PER SECOND)

FIG. 17 EFFECT OF FREQUENCY ON DYNAMIC MODULUS

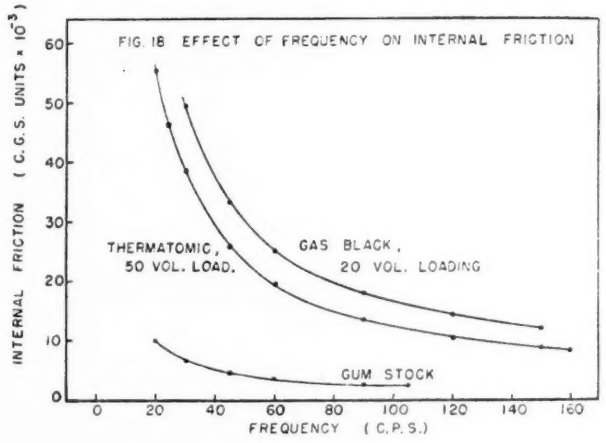


FIG. 18 EFFECT OF FREQUENCY ON INTERNAL FRICTION

CONCLUSIONS

Dynamic properties are specific for different pigments. Curves show the dependence on pigment loading of the dynamic modulus, ratio of dynamic to static modulus, internal friction, dynamic resilience, and calculated relative heat generation at constant force and at constant amplitude.

For the same volume loading, the dynamic modulus and internal friction rank in the order: Superspectra, channel black, zinc oxide, clay, blanc fixe, Therma-

tomic black, *i.e.*, roughly in the order of particle size. The calculated dynamic resilience depends on the ratio of the modulus to the internal friction and increases in the order Superspectra, channel black, clay, Thermatomic black, blanc fixe, zinc oxide. The dynamic modulus shows an almost linear relation with the internal friction for different loadings of the same pigment.

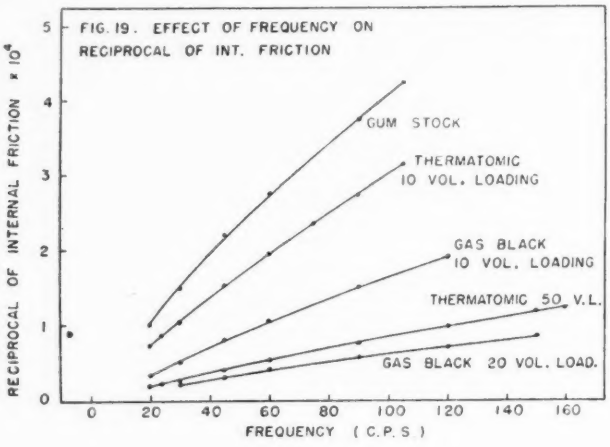


FIG. 19. EFFECT OF FREQUENCY ON RECIPROCAL OF INT. FRICTION
RECIPROCAL OF INTERNAL FRICTION × 10⁴
GUM STOCK
THERMATOMIC 10 VOL. LOADING
GAS BLACK 10 VOL. LOADING
THERMATOMIC 50 V.L.
GAS BLACK 20 VOL. LOAD.
FREQUENCY (C.P.S)

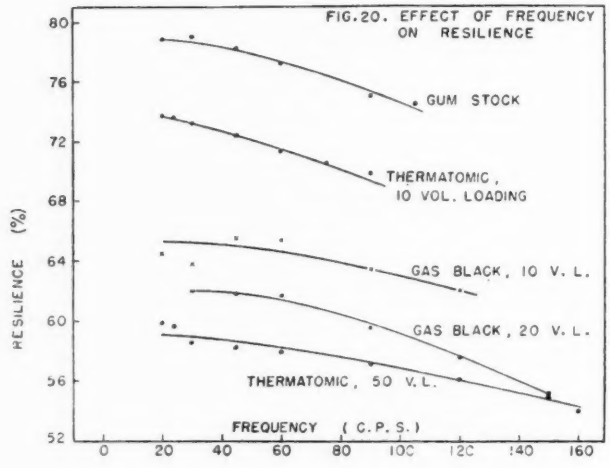


FIG. 20. EFFECT OF FREQUENCY ON RESILIENCE
RESILIENCE (%)
GUM STOCK
THERMATOMIC, 10 VOL. LOADING
GAS BLACK, 10 V. L.
GAS BLACK, 20 V. L.
THERMATOMIC, 50 V. L.
FREQUENCY (C. P. S.)

The dynamic modulus is independent of the frequency in the range 20-150 cycles per second. It depends on the amplitude, an effect which may be connected with the warming of the test-piece due to the vibration. The amplitude at resonance for the same driving force is approximately constant at all frequencies for a given rubber compound.

The results show the wide range of dynamic properties obtainable with different pigments, and bring out the general principles involved in their use for dynamic purposes.

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STUDY OF ELASTIC RELAXATION BY A RESONANCE METHOD *

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OBJECTS OF THE WORK

Elastic relaxation is one of the characteristic properties of an amorphous substance. It has been shown[1] that this effect is most easily observed in high-polymeric compounds, *e.g.*, rubber, resin, and ebonite, while observation is somewhat more complicated in polymers such as rosin. In monomeric systems, elastic relaxation is masked by viscous flow. Elastic relaxation is generally associated with the circumstance that two values must be distinguished for the modulus of elasticity of amorphous substances. One modulus is of greater value than the other. The temperature of transition from the one modulus to the other depends on the duration of the external influence or frequency of the alternating force, as well as on the chemical composition and molecular structure of the amorphous substance.

The object of the present investigation was to study elastic relaxation under mechanical influence at sound frequencies. High-polymeric ebonite was chosen as the object of investigation. The low temperature coefficient of viscosity is characteristic of ebonite.

Owing to this circumstance, elastic relaxation may be observed in ebonite over a fairly wide range of temperatures. In amorphous substances in which the temperature coefficient of viscosity is large, it would be too complicated to carry out the measurements by the method described below, since the dimensions of the specimen would change considerably on heating.

DESCRIPTION OF THE METHOD AND APPARATUS

Resonance oscillations of the specimens over a range of 3×10^2 to 7×10^3 Hz were used for the determination of the modulus of elasticity and the losses. A schematic diagram[4] of the apparatus is given in Figure 1. g_1 and g_2 are high-frequency generators with self-excitation on a wave-length of 1400 meters. The valves used for the generators were types UB-110 and UB-132, with a plate voltage of 160 V and filament voltage of 4 V. C is a variable condenser, and the whole sound-frequency range can be obtained by variation of its capacity. The frequency was measured with an electromagnetic vibration type frequency meter. The self-inductance L connected the generators with the low frequency amplifier I in which sound frequency beats were obtained. The low frequency amplifier I consisted of a three-watt resistance amplifier with all supply from the alternating current circuit. T_1 and T_2 are telephone electromagnets. The winding of the electromagnet T_1 was supplied with sound-frequency current, that of T_2 was connected to a second low frequency amplifier similar to the first one, and the voltage at the far end of this was measured on a valve type voltmeter AV. The specimen A, the elastic properties of which were to be determined, was situated and fixed in the position shown diagrammatically in Figure 1. The

* Reprinted from *Technical Physics of the USSR*, Vol. 5, No. 11, pages 842-847, 1938.

specimens were in the form of circular rods. Electromagnetic excitation was used for investigation of the resonance oscillations of the specimen. For this purpose, tips of soft iron were made for the rod, and the electromagnets T_1 and T_2 were fastened in special devices, making it possible to adjust the distance between the poles and the tips to that necessary for excitation. The magnitude of this gap was not always constant, but varied between 0.5 and 1 mm. To make the adjustments possible, T_1 was supplied with a support and T_2 with a table mounted on three adjusting screws. After the specimen and the telephone electromagnets had been adjusted, the capacity C was altered, thus altering the frequency of the alternating current feeding T_1. As soon as the frequency coincided with the natural frequency of the specimen, its amplitude increased considerably, and the magnetic field in T_2 changed, owing to the change in the e. m. f. induced in it. The frequency of this latter e. m. f. coincided with the frequency of oscillation of the specimen. The condenser reading corresponding to maximum deviation of the galvanometer G was observed. The natural frequency of oscillation of the object was thus determined. Since the specimen was clamped firmly in the center, this corresponded to excitation of longitudinal

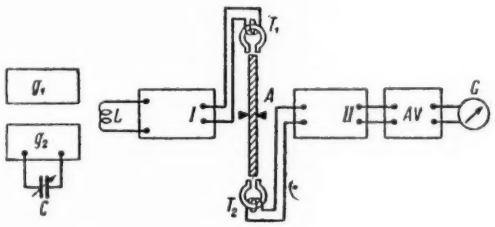


FIG. 1.

oscillations on the fundamental tone. Under these conditions the modulus of elasticity of the rod can be calculated from the well known formula:

$$E=\frac{4l^2\rho\nu_0^2}{(n+1)^2}, \tag{1}$$

where E is Young's modulus, l is the length, ρ is the density, ν_0 is the frequency, and n is the number of the overtone.

The logarithmic damping decrement served as a measure of the losses during oscillation; it can, of course, be found from:

$$\Delta=\ln\frac{An}{A_{n+1}}, \tag{2}$$

where A_n and A_{n+1} are two successive amplitudes of oscillation. To determine Δ, we used the method of resonance curves. Measurements of the relation between the modulus of elasticity and the temperature were carried out in an electrical furnace consisting of a copper cylinder. The rod was situated on the axis of this cylinder, and was fixed in this position by a holder in the center of the tube. This holder consisted of two iron prisms, one of which was immovably fastened to the wall of the tube, while the other could be moved perpendicular to the axis of the cylinder by means of a screw. The furnace containing the specimen was set vertically, and the temperature of the specimen was measured by two thermocouples fastened to it, one at the top and the other at the bottom.

RESULTS OF THE OBSERVATIONS

The table gives the results of measurements carried out on five specimens at $t=19°$ C.

Certain remarks may be made about the data given in the table. The results obtained for E and Δ show that relaxation is not observed over the entire frequency range given in the table. It is not possible to determine the elastic relaxation time of ebonite accurately at room temperature, but it is very great, *viz.*, some millions of seconds[1]. It should be noticed that the damping decrement of ebonite made out of natural rubber is 40 per cent less than when it is made of synthetic rubber, which cannot be explained by errors of measurement.

TABLE I

Specimen No.	Ebonite	Length of rod (cm.)	Herz	$E \cdot 10^{-4}$ kg. per sq. cm.	$\Delta \cdot 10^{2}$	Remarks
1	Of natural rubber..	19.9	3824	2.86	6.0	Longitudinal oscillations on fundamental tone
2		44.4	1707	2.88	6.1	
3		93.0	830	2.94	4.8	
4	Of synthetic rubber	28.0	2784	2.98	8.7	
5		70.2	1145	3.16	8.3	
5		70.2	2317	3.24	—	1st overtone
5		70.2	3488	3.26	—	2nd overtone
5		70.2	4643	3.24	—	3rd overtone
5		70.2	5839	3.28	—	4th overtone
5		70.2	6876	3.16	—	5th overtone

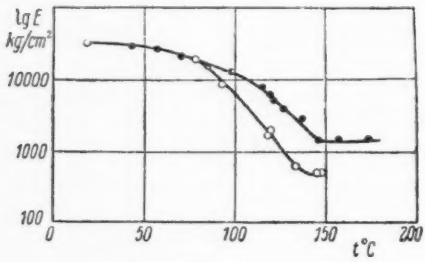


FIG. 2.

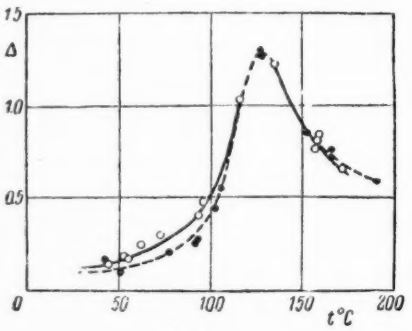


FIG. 3.

Changes in the fastening of the rods had no considerable effect on the magnitude of the decrement. The error in measuring the decrement was of the order of 10 per cent, and in the determination of E of the order of 3 per cent. The values given in the last line of the table are averages of a number of observations. The influence of the temperature was studied on specimens 4 and 5. Figure 2 gives the results of the observations on specimen 5 only. The modulus E was determined from the resonance frequency of oscillations on the basic tone, which means that in Equation (1) it is necessary to make $n=0$. The curve with points denoted by white circles relates to the first heating of the specimen to a temperature of 150° C; the curve with points denoted by black circles corresponds to subsequent heating above 150° C. These measurements were carried out at both raised and reduced temperatures. Repeated measurements gave results which always fell on the curve denoted by black circles. The same effect was observed for specimen 4.

The changes in the value of the modulus at high temperatures are shown in Figure 2 and the changes in the character of the curve after the first heating may be explained by a process of additional vulcanization. This process consists of a chemical reaction between mechanically dispersed sulfur and polymeric molecules of rubber[3]. The vulcanization temperature of our specimens of ebonite was 140° C. It was noticed that when the heating was carried out to less than 140° C, the curve of the temperature function of the modulus E followed the curve denoted by the white circles. On heating to above 140° C, a part of the free sulfur could react and produce additional vulcanization. Measurements of the damping decrement were carried out at the same time as the measurements of E. Figure 3 gives two curves with the decrement laid out on the ordinate.

The curve shown by a full line with points denoted by white circles relates to specimen 5; the dotted curve with black points to specimen 4. The resonance frequency of specimen 4 at room temperature is 2.42 times greater than that of

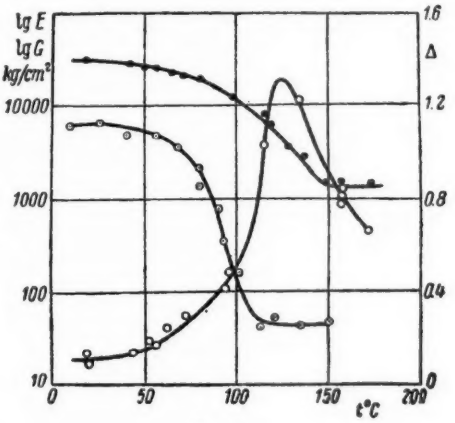


Fig. 4.

specimen 5. A displacement is observed in the positions of the maximum decrements, even though the difference in the frequencies is so small, the curves being displaced in the manner required for the relaxation mechanism of losses. To separate the curves more sharply, it is necessary that the natural frequencies of the rods should differ by 20-30 times. Unfortunately, when the frequency was changed twentyfold, the frequency characteristic of the amplifier had 60 per cent choke. This circumstance made it difficult to take the resonance curves. To illustrate the results obtained in the work more graphically, we have given together on Figure 4 curves of E, Δ, and G, the torsion modulus as functions of the temperature, as obtained by the static method[1]. The left-hand ordinate gives log E and log G, and the right-hand one the decrement. The temperature in degrees centigrade is given on the ordinate. The curves of E and G are similar in nature, the principle difference lying in the temperature at which the modulus falls rapidly. The combination of a sharp fall in E and anomalous changes in the losses is characteristic of relaxation mechanism effects. According to the maximum decrement of Figure 4, the transition temperature at which ebonite becomes elastic is 127° C at a frequency of 600 Hz. The transition temperature of ebonite as found from static measurements is 80° C, corresponding to a time of establishment of elastic deformation of the order of 10^4 seconds. From the

relationship $\omega\tau=1$, which connects the relaxation time with the frequency, it will be seen that displacement of the temperature of the elastic state by 47° C corresponds to a change of 10^7 times in the relaxation time. Both the nature of the temperature functions of E, G and Δ and the evaluation of the relaxation time only give the basis of a solution of the problem of the mechanism of the effect. As far as the details are concerned, it is, of course, necessary to take into account the influence of the amplitude and the viscosity. Molecular transformations are possible with large deformations, and these may be determined by the intensity of the external influence. These irreversible transformations should depend very little on the temperature. It is well known that with amorphous substances, the relaxation mechanism of losses is observed in the case of electrical as well as mechanical influences.

The mechanical losses in ebonite at room temperature are about 10^2 times greater than the dielectric ones.* These large losses may possibly be unconnected with relaxation, but depend on the amplitude of the oscillations.

SUMMARY

The present work gives the results of measurements of the modulus of elasticity and the losses in ebonite by a resonance method. These magnitudes are determined as functions of the temperature for two specimens. At $t=19°$ C, the resonance frequency of one of the specimens was 2784 Hz, of the other 1145 Hz. At these frequencies and higher temperatures ebonite is highly elastic. It is shown that the transition to this state at sound frequencies takes place at a temperature 47° C higher than by the static method.

REFERENCES

[1] Kobeko, Kuvshinskij and Gurevich, *Tech. Phys. USSR* **4**, No. 8, 1937.
[2] Walter and Wegel, *Physics* **6**, 141, 1935.
[3] Houwink, "Elasticity, Plasticity and the Structure of Matter," Cambridge, **1937**.
[4] A similar method was used by Wegel and Walter in studying the internal friction in metals.

* The dielectric losses of ebonite were measured on a Wien sound bridge. It was only found possible to determine their order of magnitude, namely $\tan\delta \sim 10^{-4}$.

THE TEAR RESISTANCE OF RUBBER COMPOUNDS *

G. A. Patrikeev and A. I. Melnikov

For some time it has been recognized that one of the most important properties governing the usefulness of a rubber article is its ability to resist tearing[1]. Since this property bears no direct relationship to tensile strength[2], it is often necessary to make special determinations of tear resistance. Since 1922, various methods for measuring tear resistance have been suggested. Unfortunately the results obtained by these methods differ greatly, and cannot easily be compared[3, 4].

The object of the present investigation was to study the tear resistance of both natural and synthetic rubbers[5], and to find a method of determining it more consistently and more accurately.

Present methods of measuring tear resistance can be divided into three groups:

I. Direct tearing.
II. Tearing perpendicular to the direction of stretching.
III. Tearing of samples sliced in the direction of stretching.

I. Group I includes the methods of Zimmerman (Figure 1a), Evans (Figure 1b), Heidensohn (Figure 1c), Lefcaditis and Cotton (Figure 1d), Talalay (Figure 1e), Marzetti (Figure 1f) and Kusov (Figure 1g)[3, 4, 6, 7, 8]. The method used by Wright (Figure 1h) is intermediate between those of the first and second groups. The test-specimens used for these methods vary from 1 to 6 mm. in thickness.

II. Group II includes the method of Winkelmann, which has been adopted as standard in the U.S.S.R. (Figure 2a), that of Busse (Figure 2b), that of van Rossem and the identical one of van Wijk (Figure 2c), and the method of Davies[9, 10, 11]. The test-specimens used for these methods vary in thickness from 0.5 to 6 mm.

It appears that the values of tear resistance obtained by direct tearing (group I) are much smaller than those obtained by the methods of group II.

The methods of the second group have the advantage over those of the first in that they enable a certain degree of comparison between tear resistance and tensile strength, which is not possible by the methods of group I.

It should be remarked that none of these methods gives consistent results; for example, measurements by the Goodrich method have an average deviation of 8 per cent, and the method of Wright yields values which vary 9 per cent.

III. The method of group III. Tear tests were conducted on specimens cut in the direction of stretching. For this purpose strips $180 \times 10 \times 1$ mm., with a central longitudinal cut beginning at one end and 80 mm. long, were prepared. The uncut end of the specimen was held in the top clamp of a Scott dynamometer. The other two ends were held in clamps which could be moved horizontally along a bar which was attached to the bottom clamp of the dynamometer. With this device, it is possible to stretch the specimen and, at the same time, to separate the legs of the test-piece to any required angle (Figure 3).

* Translated and edited by J. Talalay for Rubber Chemistry and Technology from *Caoutchouc and Rubber* (U.S.S.R.), pages 12-20, December 1940.

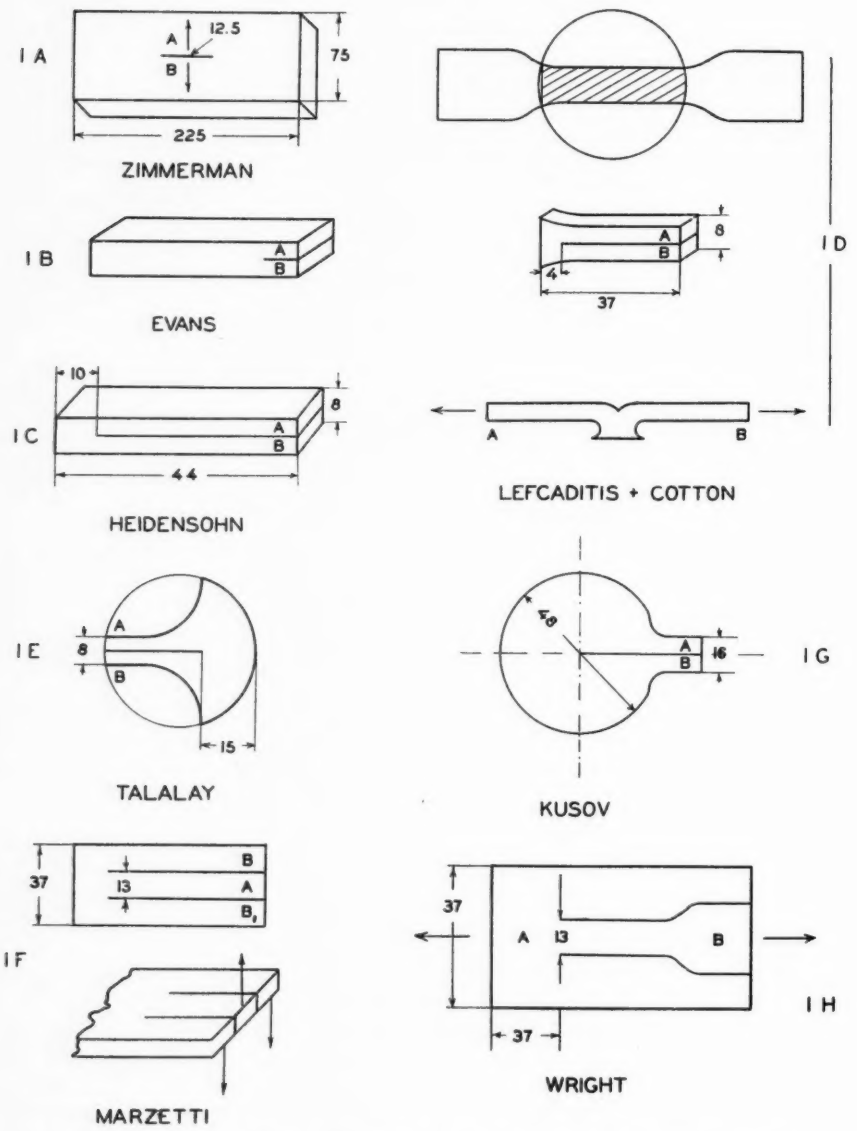
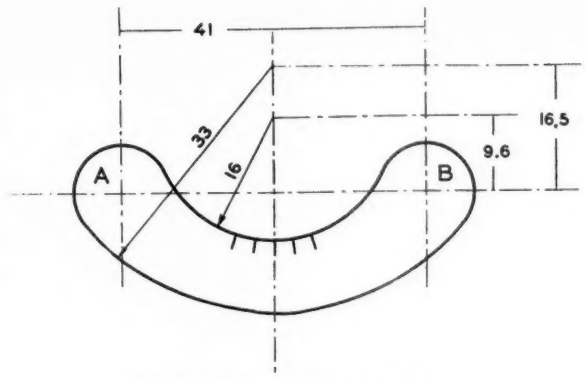
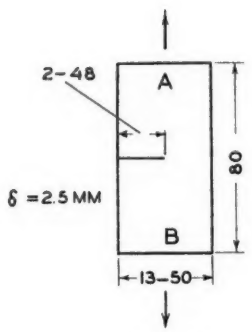


FIG. 1.—Determinations of tear resistance by methods of group I. (All dimensions in mm.)



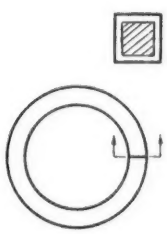
GOODRICH - WINKELMANN

2A



BUSSE

2B



VAN ROSSEM
VAN WIJK

2C

FIG. 2.—Determinations of tear resistance by the methods of group II. (All dimensions in mm.)

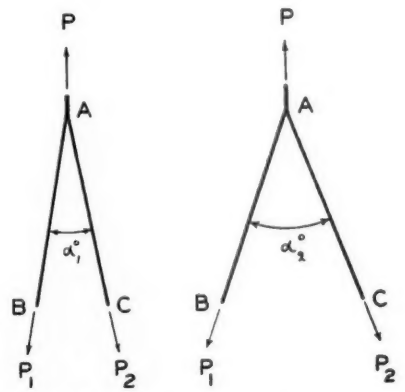


FIG. 3.—Diagram for method of group III, showing determination of angle α.

Let $\alpha°$ be the angle between the legs of the stretched specimen when it begins to tear. For a given tension, α has a definite value which depends on the quality of the specimen. All other conditions being equal, the greater the angle α, the greater is the tear resistance.

To compare the tear resistance of different rubber compounds, similar specimens were prepared, and α was determined at different tensions. The procedure was as follows. The test-specimen was stretched to a definite dynamometer reading, and the cut ends were then moved apart until tearing began. The angle α at the moment of tearing was determined, either by direct measurement or indirectly from a photograph (Figure 3). The procedure was repeated not less than three times for each load, and the average angle α, the criterion of tear resistance, was plotted against the various loads.

I. EXPERIMENTAL PART

Samples of synthetic and natural rubber compounds were prepared on laboratory mixing mills, and their tear resistances were investigated by a method of the second group. Sheets 1 mm. thick were vulcanized in moulds, and rectangular specimens, $90\times16\times1$ mm., were cut out. The thicknesses of the specimens were determined by a micrometer. In the region where the cut was made, this thickness was 1 ± 0.02 mm. The incision was made with a razor blade perpendicular to the edge of the specimen, and the depth of the cut was measured under magnification. For every set of experiments, three test-pieces were prepared, with cuts 0.5 mm., 1 mm., and 3 mm. deep.

The specimens were tested on a Scott dynamometer, running at normal speed. For greater sensitivity, the dynamometer was calibrated without the additional weight. Dynamometer readings were in kilograms, and the tear resistance σ_z was expressed according to the formula:

$$\sigma_z = \frac{P}{\delta} \text{ kg. per cm.}$$

where P is the load in kilograms at the moment tearing begins, and δ is the original thickness of the sample in cm.

Different Factors Influencing Resistance to Tearing

A. *Thickness.*—The tear resistances of carbon black compounds made from synthetic and natural rubbers were measured with samples of different thicknesses. Experiments show that tear resistance increases with increase in thickness. Figure 4 shows the relation between tear resistance and thickness for a constant depth of cut (2 mm.). With increasing thickness, the tear resistance rises rapidly at first (to about 2.5 mm.), and then more slowly. Similar observations were made with samples of both natural and synthetic rubbers.

B. *Speed of Stretching.*—Figure 5 shows the relation between the speed of stretching and the tear resistance of samples of synthetic rubber containing carbon black. In this diagram, as in the later ones, tear resistance is plotted as a function of the depth of cut. It was observed that, for rates of stretching in the range of 200 to 600 mm. per min., there was little change in the tear resistance, whereas the effect was more pronounced at higher and lower speeds.

C. *Angle of Cut.*—The angle between the cut and the edge of the specimen is an important factor in the measurement of tear resistance. To prove this, cuts were made at different angles β (Figure 6a). If the shape of the cut on

the edge of the sample is halfround instead of straight (Figure 6b), considerably higher tear resistance is obtained. It should be noted here that, as in the case of a straight cut, there is a concentration of tensile strain at the deepest part. This tensile strain, which is the cause of tearing, is smaller for a halfround than for a straight cut of the same depth, and increases as the radius of the halfround becomes smaller.

D. *Depth of Cut and Supplemental Cuts.*—

(a) The depth of cut has no significant influence on tear resistance measured by methods of the first group, but is a decisive factor in determinations by any

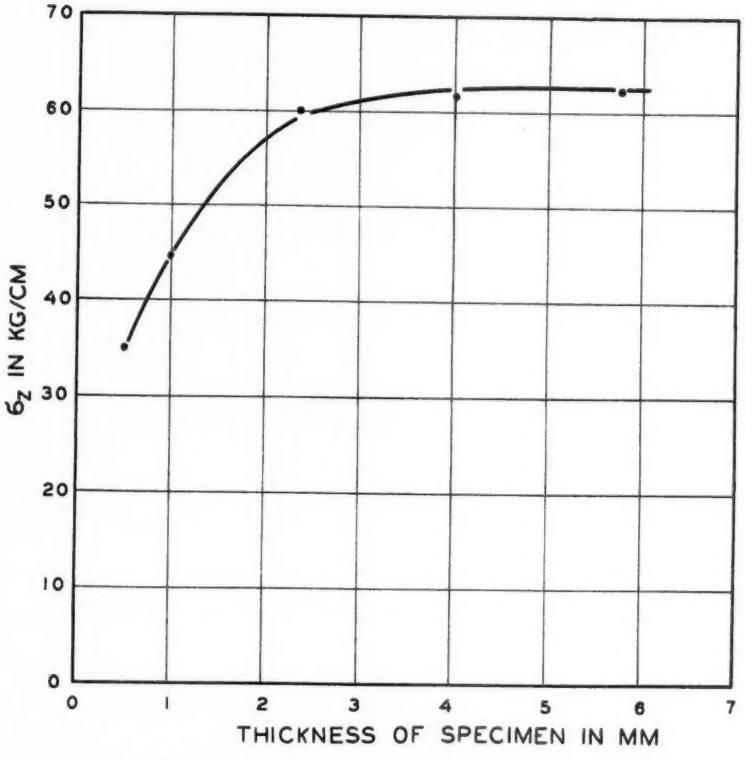


FIG. 4.—Relation between tear resistance and thickness of specimen.

of the methods of the second group. It is, therefore, of paramount importance to determine accurately the depth of cut when employing any method of group II. The relation between tear resistance and depth of cut is shown in Figures 5, 9, 10 and 11.

(b) At the base of the normal cut a supplementary incision was made perpendicular to the direction of the first cut (Figure 7a). When tested, such a sample undergoes a greater degree of deformation in the narrower middle part (Figure 7b) than a sample with only a single cut. The free wings that have been formed point in opposite directions at an angle of about 60°. The tensile force required to tear such a sample is considerably larger (almost twice as great) as with one original cut. The specimen tears crosswise at one of the extremities of the vertical (supplementary) cut (Figure 7c).

(c) If the vertical cut is made to intersect the original cut (Figures 7d and 7e), the specimen tears along the direction of the original cut. In this case, the tear resistance is larger than with a single original cut, but smaller than in case (b).

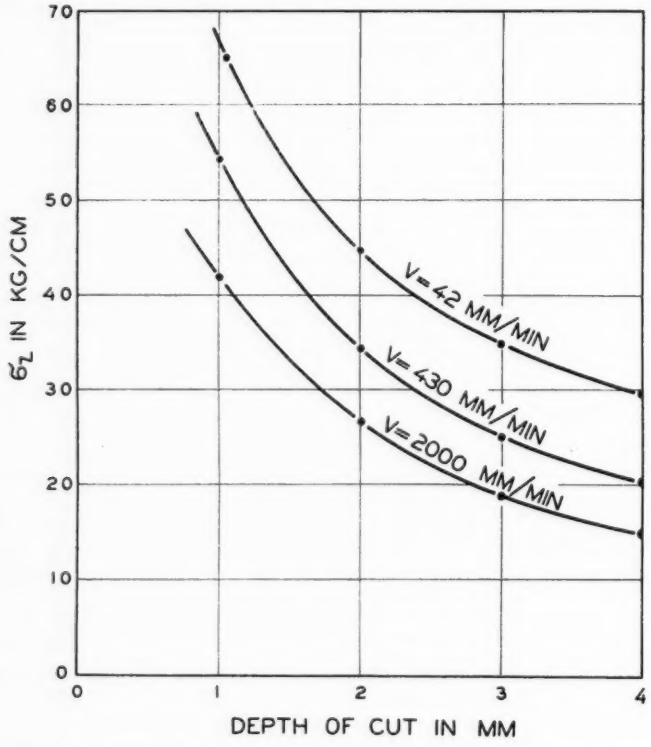


FIG. 5.—Relation between tear resistance and depth of cut at various speeds of stretching.

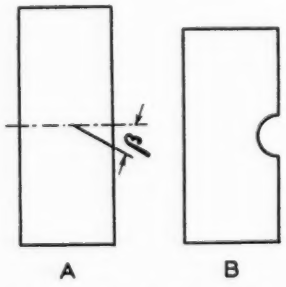


FIG. 6.—Angle and shape of cut made in test-pieces.

(d) A supplementary cut parallel to the original cut and in its immediate proximity (Figure 8a) increases the tear resistance. Likewise, the tear resistance increases if a supplementary cut is made on the specimen on the opposite side from, and in line with, the original cut (Figure 8b). In both cases, the increase

in tear resistance of the specimen produced by the introduction of parallel supplementary cuts can be explained by a reduction in deformation at the bases of the cuts.

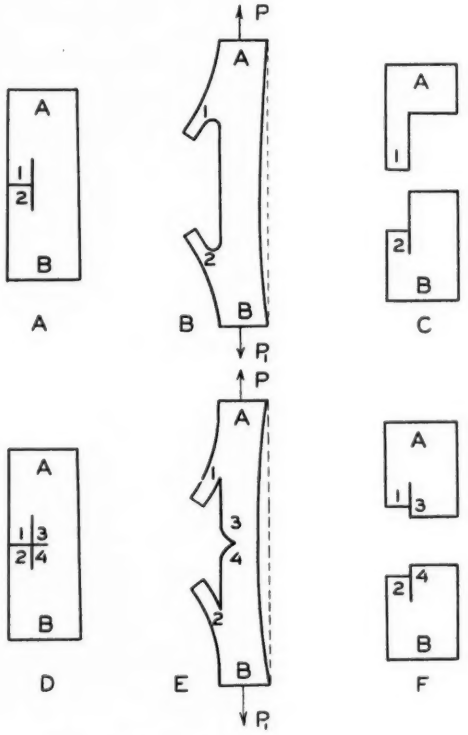


FIG. 7.—Effect of supplementary cuts on the tearing of specimens.

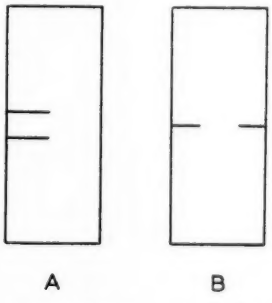


FIG. 8.—Effect of supplementary cuts parallel to original cut.

E. *Vulcanization and Type of Compound.*—The relation between tear resistance and degree of vulcanization was investigated for synthetic rubber compounds. For this purpose a compound containing 60 per cent of carbon black was prepared, with 2-mercaptobenzothiazole as accelerator. This compound was vulcanized in a press for 10, 20, 40 and 60 minutes at 3 atmospheres' steam pressure.

The results of tear resistance tests are recorded in Figure 9. This shows that the tear resistance at first rises rapidly with time of vulcanization, reaches a maximum at 18-20 minutes, and then drops sharply. The maximum tensile strength of the same compound is, however, reached only after vulcanizing for 40-45 minutes.

A natural-rubber compound of the same composition reaches its maximum tear resistance after a 10-minute cure, and maximum tensile strength only after 25 minutes. This was found to be true of synthetic rubber compounds containing kaolin.

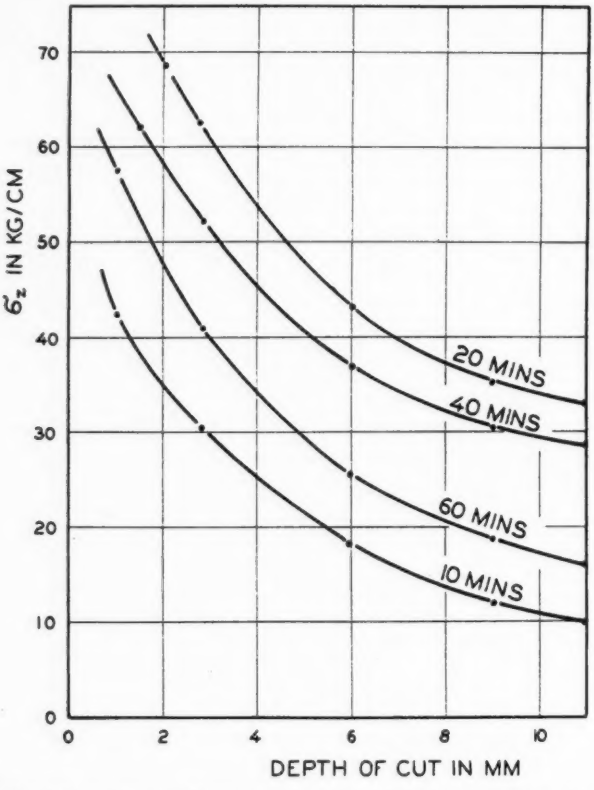


FIG. 9.—Relation between tear resistance and depth of cut for various times of vulcanization.

As a rule, when considerably undervulcanized, compounds have much higher tear resistances than the same compounds vulcanized to give maximum tensile properties. The time difference between the two maxima depends largely on the compound, and is governed by the proportion and type of accelerator. The use of a greater proportion of accelerator or of more powerful accelerators decreases the time interval between maximum tear resistance and maximum tensile strength. Under no circumstances, however, is maximum tensile strength attained before maximum tear resistance.

F. *Carbon Black.*—The tear resistances of synthetic rubber compounds containing 30, 40 and 60 parts of carbon black are shown in Figure 10. It is evident that tear resistance increases with the carbon black content. Even with

70 parts of carbon black, the tear resistance still continues to increase. This is in entire agreement with results obtained with natural rubber compounds[9]. Kaolin and magnesium oxide increase only slightly the tear resistance of synthetic rubber compounds.

G. *Types of Rubber.*—The tear resistances of compounds made with pale crepe, Kok-Sagyz (grown in the U.S.S.R.), and synthetic rubber were compared. These compounds contained 60 per cent of carbon black, and 2-mercaptobenzothiazole was used as accelerator. Figure 11 shows the tear resistances of these compounds plotted against the depths of cut. It should be pointed out that the

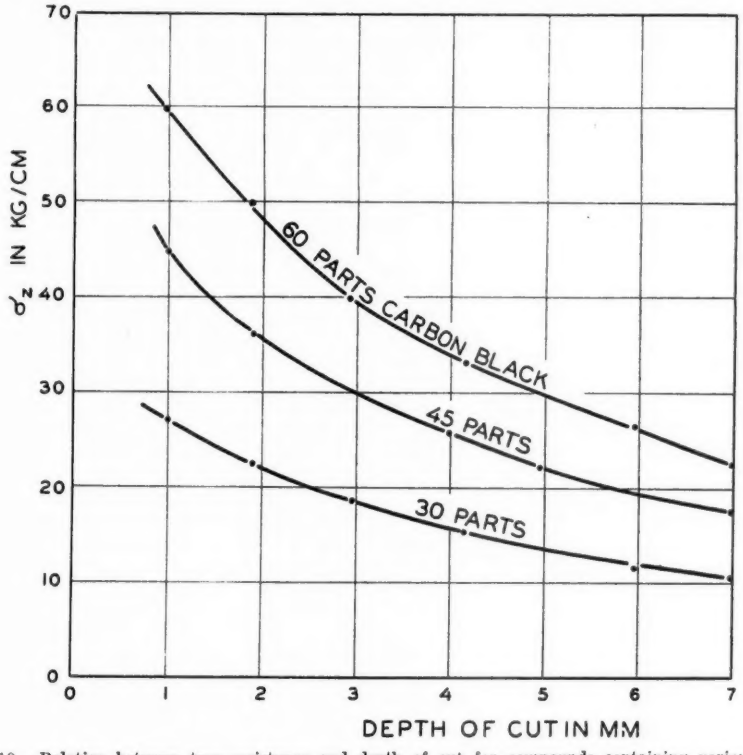


FIG. 10.—Relation between tear resistance and depth of cut for compounds containing various proportions of carbon black.

tear resistance of synthetic rubber is lower than that of natural rubber. This difference is more pronounced for short cuts, and decreases as the cut is made longer. Furthermore, the decrease in the tear resistance of natural rubber with increasing depth of cut is more rapid than is the decrease in tear resistance of synthetic rubber. This is confirmation that the mechanism of resistance to tearing of natural rubber is different from that of synthetic rubbers.

II. DISCUSSION OF THE RESULTS

A rubber specimen tears when there is a consecutive rupture of the structural elements in immediate proximity to the cut at the point where the specimen undergoes the greatest deformation[10, 11]. Therefore the basic requirement for

tearing to occur is a sufficiently great local deformation of the material. Measurement of the deformation of a specimen being stretched shows that the specimen is always thinnest at the base of the incision. Depending on the method of stretching and the shape of the test-piece, one of three types of deformation occurs (Figures 12, 13, 14). The forces causing deformation of the specimen are P and P_1; the forces appearing as the result of the presence of the cut are Q and Q_1. It is these forces which are the cause of tearing. The original mean thickness of the sample is δ while δ' is the thickness at the point of maximum deformation.

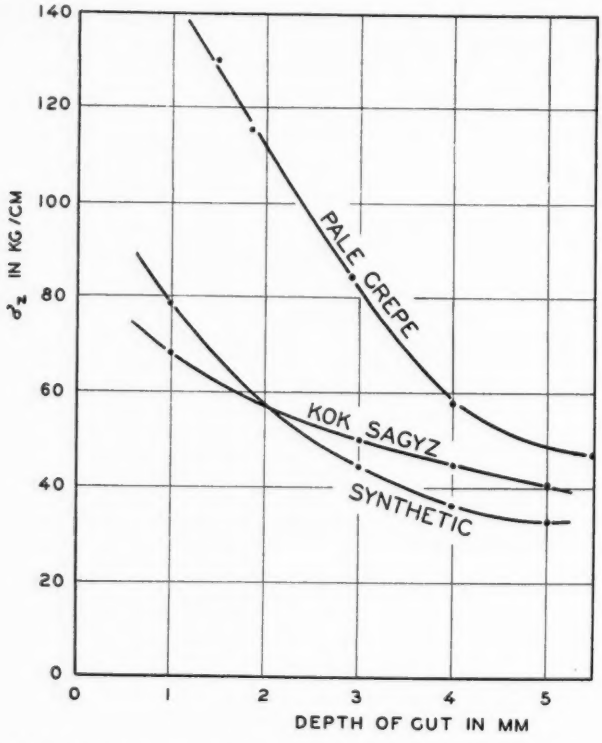


FIG. 11.—Relation between tear resistance and depth of cut for various types of rubber.

A. For methods of group I, the distribution of forces and decrease in thickness of the sample are shown in Figure 12.

Different sections of the specimen undergo varying degrees of deformation; one side of the specimen is considerably more deformed than the other. In this case the forces causing deformation, P and P_1, act almost in the same direction as the forces, Q and Q_1, which bring about tearing. Q and P are simply related, thus: $Q=f(P)$. The side view (Figure 13b) shows the region of minimum thickness of the specimen. The relation between δ and δ' depends on the general mechanical properties, such as the modulus of the rubber.

B. For methods of group II, to which we have devoted most of our attention, the deformation of the specimen is shown in Figure 13. Figure 13b is a side view of a sample under deformation, both by methods of group I and group II.

In this case forces, P and P_1, and Q and Q_1, no longer coincide in their direction, and Q is a function of both P and n $(Q=\phi(P,n))$, where n is the depth of the cut.

When all forces are in equilibrium, the uncut edge of the specimen assumes a characteristic bend caused by forces Q and Q_1.

C. Specimens tested by the method of group III (cut longitudinally) undergo deformation as in Figure 14. The minimum thickness of the specimen δ' and the tearing force Q are functions of the angle $\alpha°$ and the deforming force P, so that $Q=\phi'(P,\alpha°)$.

In the three cases considered above, we observe the following facts:

The actual tearing force Q is directed along the surfaces formed by the tear. The relation between forces P and Q is different in each of the three cases (A, B and C).

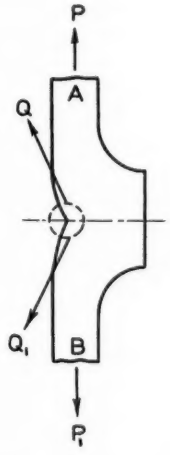


FIG. 12.—Diagram of Deformation of sample tested by methods of group I.

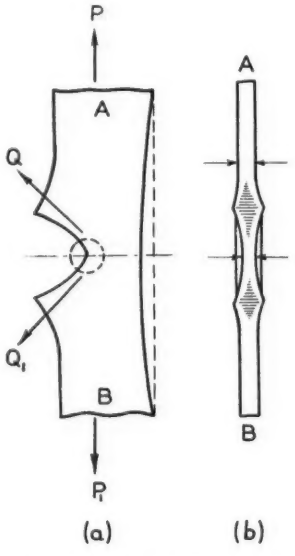


FIG. 13.—Diagram of Deformation of sample tested by methods of group II.

The maximum deformation of a specimen occurs, in every case, at the base of the cut.

The deformation decreases in all directions away from the cut.

Finally, it is a well established experimental fact that the degree of maximum local deformation required to bring about tearing is less than the critical deformation of a sample about to break in a tensile test[9]. This suggests the presence of some other factor which weakens the elastic material at the base of the incision. It does not seem possible to explain the phenomenon of tearing solely by a maximum deformation at the end of the cut, without postulating that a local weakness occurs in the material at the place of tearing.

The most likely concept to explain this phenomenon is that the elastic deformation of rubber is accompanied by an orientation effect. The bonded internal structural elements of the rubber are assumed to undergo relative displacement, which causes the structure to become anisotropic in the direction of stretching. The degree of orientation increases with increase in the deformation.

Since the maximum deformation occurs at the end of the cut, and since deformation decreases in all directions away from the cut, it must be assumed that the structural elements have the greatest degree of orientation in the surface layers in immediate proximity to the cut.

In all three cases, the orientation process is caused by the forces Q and Q_1. The structural elements of the most deformed part at the base of the cut become oriented in two directions parallel to the lines of action of forces Q and Q_1 (Figure 15). The apex of the angle γ between the two directions lies at the base of the cut. As the edges of the specimen are stretched further, they gradually pull along with them the less deformed elements lying immediately behind the base of the cut in the region C_1OC_2 (Figure 15).

As a result of this process of structural surface orientation in two directions at angle γ, the material becomes weak in the vicinity of the dividing line of the two directions of orientation. It is here that tearing begins under certain conditions of deformation.

In view of the fact that the formation of new surfaces which are formed in the process of tearing is conditioned both by the weakness of the the material at the cut and by the degree of local deformation, it was interesting to investigate the direction of the resulting tear with the object of further elucidating the mechanism of tearing.

Generally speaking, there are two types of tear which are encountered with different rubber compounds:

(1) *Smooth,* straight tearing in the direction of the original cut, or at a slight angle to it.

(2) *Knotty,* zigzag tearing, whereby the specimen exhibits a definite tendency to tear at right angles to the direction of the original cut, *i.e.,* in a direction parallel to the stretching forces.

With the majority of rubber compounds, smooth, straight tearing occurs at low rates of tearing, and invariably at high velocities[9].

If a tough rubber compound containing carbon black is stretched slowly, changes in the direction of the tear are observed immediately after tearing begins, and a knotty effect is obtained.

Future investigations along the lines of the ideas expressed above will undoubtedly prove that the change in the direction of tear is due to structural orientation, and will thereby assist in formulating a more complete theory of the strength of elastic materials.

The change in the direction of tear which usually occurs at right angles reduces considerably the local deformation, and the specimen thus undergoes a reinforcing effect. When a new tear appears, we are in fact tearing a sample with a supplemental cut and, as we have seen above, such a sample has nearly twice the tear resistance of a normal one.

It should be noted that measurements of resistance to tearing by the methods of group I are considerably more sensitive to changes in the direction of tearing than are methods of group II. This is due to the fact that, in the latter case, force Q, which causes tearing, is considerably reduced by changes in the direction of tearing, whereas in the former case this effect is much smaller. Nevertheless, whatever the method, a change in the direction of tear gives an increased value for σ_z (fictitious). It appears, therefore, that the enormous increase in tear resistance of rubber specimens with knotty tears is partly imaginary, and must be attributed to the inadequacy of the testing technique adopted.

The truth of this observation was demonstrated by a sample of synthetic rubber containing carbon black, which exhibited knotty tearing. In one experi-

ment, the initial tear resistance at the beginning of tearing was $\sigma_z = 10.4$ kg. per cm., while the maximum reached was $\sigma_z = 22$ kg. per cm. This is explained by the fact that the direction of tearing changed in the course of the experiment. The depth of cut was 3.6 mm. in all cases.

In another case, a small supplemental cut at right angles to the first one was made in a specimen which normally gave a straight tear. It was necessary to apply more than 1.5 times the normal force to produce further tearing.

This view of the mechanism of knotty tearing is borne out by the fact that, if similar samples are torn much more rapidly or at elevated temperatures, tearing

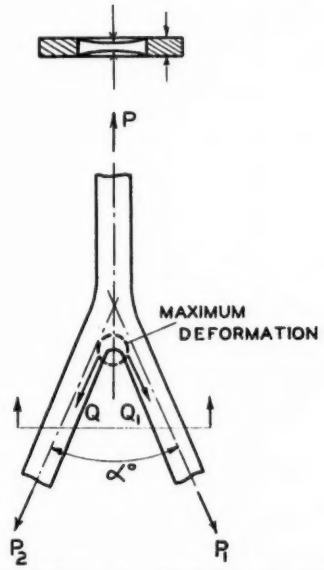


FIG. 14.—Diagram of deformation of sample tested by the method of group III.

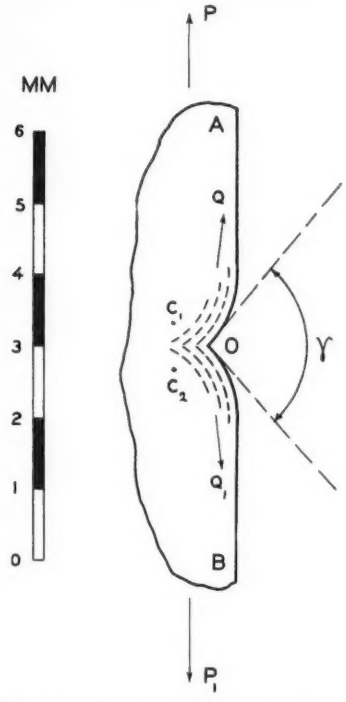


FIG. 15.—Diagram showing orientation of structural elements near base of cut.

takes place along a straight line, and the recorded tear resistances are much lower.

Further success in establishing a theory of the strength of elastic materials can be attained only by a study of the maximum deformation of stretched samples with incisions, and by an investigation of the process of structural surface orientation rendering the material weaker in the direction of future tearing.

SUMMARY

1. An improved method of measuring tear resistance was developed. The samples which were examined were cut in the direction of stretching.

2. The relation between tear resistance and time of vulcanization was investigated.

3. The tear resistances of synthetic and natural rubbers were compared.

4. It is shown that the tear resistance of samples of natural and synthetic rubber depends on the depth of the initial cut. With short cuts, natural rubber has a higher tear resistance than synthetic rubber, but this difference decreases as the cut is made longer.

5. It is established that the tear resistance of thin rubber specimens is smaller than that of thicker specimens.

6. The mechanism of tear resistance is discussed. Factors such as deformation are considered.

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STUDIES OF THE AMORPHOUS STATE

XVII. DIELECTRIC LOSSES IN SWOLLEN RUBBERS *

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Physical Technical Institute, Leningrad, U. S. S. R.

As has been shown by a number of investigators, in many cases the rate of relaxation (the rate at which polarization in amorphous dielectrics attains the equilibrium value) is proportional to the macroscopically measured viscosity of the given substance. The addition of plasticizers, *i.e.*, substances which lower the viscosity, leads to a corresponding change in the rate of relaxation; as a result, at the given frequency, the maxima of the dielectric losses are always obtained at the same values of the "viscosity". In highly polymerized compounds, the maxima are often typical for Debye losses, the value of the macroscopic viscosity being very high. This leads us to assume that the decrease in mobility of the macromolecule does not considerably affect the orientation of its separate parts in spite of the chemical bonds between them. The study of the influence of swelling on the dielectric losses in highly polymerized substances is of great interest, as it may throw more light on the question how the various solvents are distributed throughout the given polymer and whether the influence of the chemical bonds on the relaxation rate is essential for the orientation processes.

Products prepared from natural rubber containing 3 per cent of sulfur were selected for the test. Previous literature contains ample information on the dielectric losses in rubbers at different temperatures, frequencies and for various contents of sulfur. Based on these data, Müller[3] advanced his hypothesis, according to which the sulfur atoms, which in the course of vulcanization are chemically bound, form polar groups susceptible to orientation. Rubber was selected, not only because of its technical value, but as a substance with a comparatively low concentration of dipoles which can be altered at random by adding various admixtures.

The rubber specimens were immersed in different liquids: paraffin oil, toluene, turpentine and bromobenzene.

The extent of swelling was judged by the increase in weight. To determine the effect of various degrees of swelling, the given specimen was subjected to repeated swelling.

It had been ascertained by preliminary experiments that the slight dissolution of certain components which takes place under these conditions does not affect the dielectric losses; after evaporation of the solvent[7], the sample resumed its initial electrical characteristics. The swollen sample was kept for a few hours to allow the solvent to be uniformly distributed through the volume and was then weighed twice—before and after the measurement in order to control the evaporation and to apply the necessary corrections.

A substitution method (Figure 1) was applied in the preliminary tests, the frequency used being 2×10^7 Hertz; for the main measurements a bridge method at acoustic frequency was used. The capacity of the sample being about 100 cm., values of tan δ of the order of 5×10^{-4} could be readily measured, using Wien's bridge with amplification.

* Reprinted from *Technical Physics of the USSR*, Vol. 5, No. 11, pages 836-841, 1938.

The specimens were placed in the apparatus shown in Figure 2. The specimen (*2*) and the foil electrode (*3*) were rolled on the inner cylinder (*1*). The thermocouple (*4*) was built into the specimen, which was then covered by the screening cylinder (*5*) provided with an electric heater (*6*). The whole apparatus was placed in a glass cylinder or in a Dewar vessel with liquid air. By means of the heater the temperature of the apparatus could be maintained for a sufficiently long time at a given temperature ($-100°$) within an accuracy of 0.5° C. Special

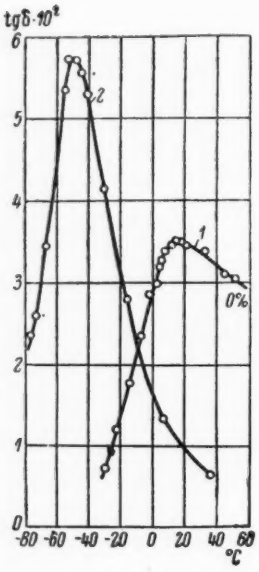

FIG. 1.

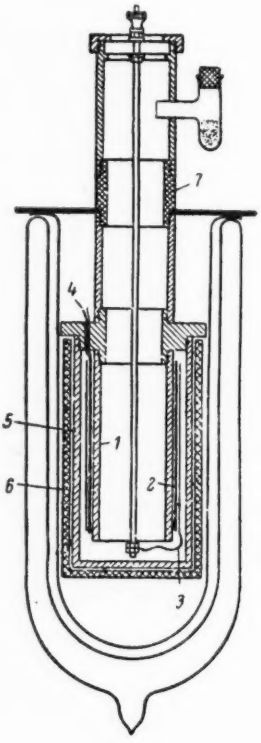

FIG. 2.

thermal insulation was provided to prevent the leads from freezing. The inside of the apparatus was dried with P_2O_5. The apparatus proved very convenient, and was used in all our experiments at high, as well as at industrial frequencies.

In the first series of experiments, swelling of the specimen took place in nonpolar paraffin oil. The results, shown in Figure 3, coincide with those obtained in preliminary experiments at high frequencies. The maximum of tan δ is seen to have shifted towards lower temperatures and its height to have decreased. It should be noted that the swollen rubber behaves like a uniform system possessing a single maximum.

The above fact would indicate that, due to the swelling, the conditions for the orientation of all the dipoles are changed in a like manner. Since these conditions are determined by the surrounding medium, it may be assumed that the distribution of the paraffin oil in the rubber is the same as that of the dipoles.

The change in the height of the maximum is evidently related to the change in concentration of the dipoles and, in a first approximation, is inversely proportional to the change in volume.

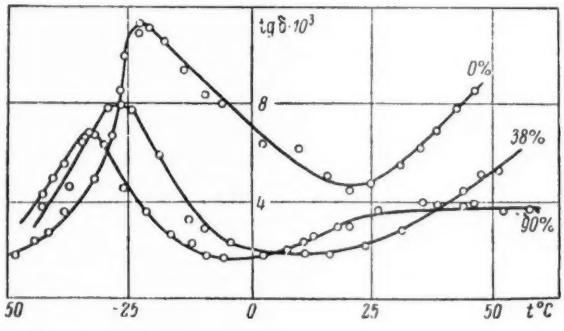

FIG. 3.

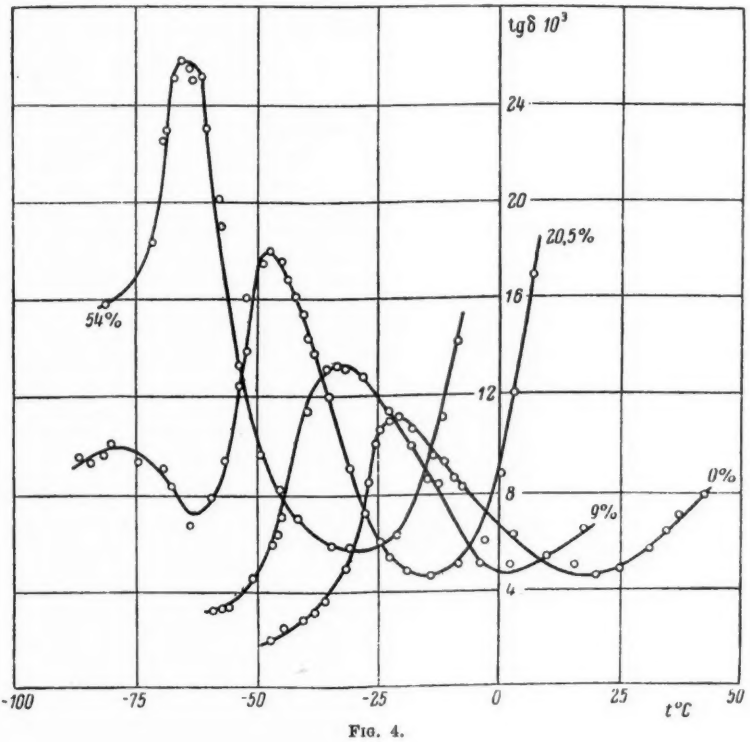

FIG. 4.

Another series of experiments dealt with the swelling of rubber in bromobenzene. As may be seen from Figure 4, the displacement of the maximum again depends on the amount of the incorporated substance. The increase in the height of the maximum points to an increase in the concentration of the dipoles,

indicating that the dipoles of bromobenzene also participate in the losses. Each curve has only one maximum, indicating that the orientation of the rubber dipoles (where they are united to the macromolecule by chemical bonds) is similar to that of bromobenzene dipoles (which are united to the neighboring particles by van der Waals forces).

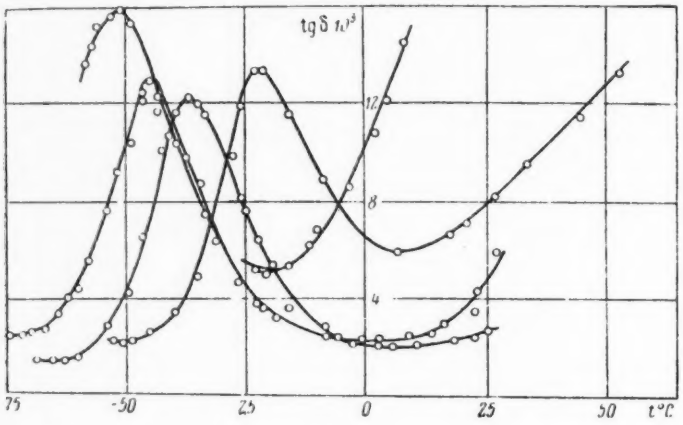

FIG. 5.

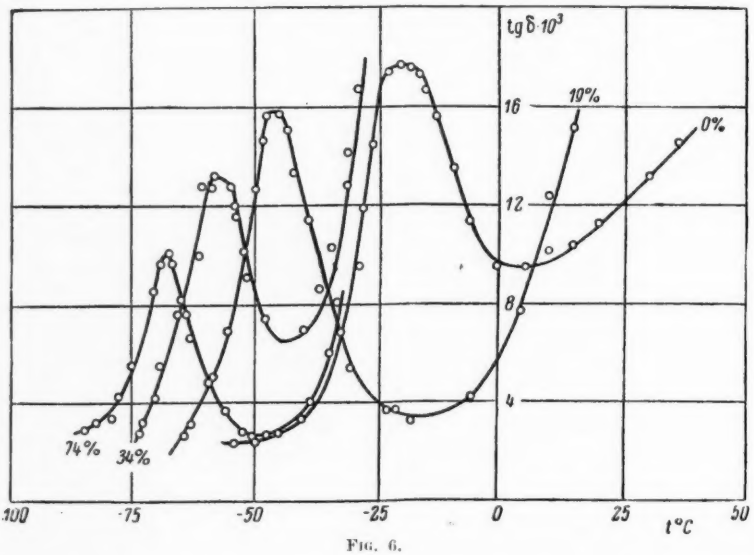

FIG. 6.

The same relationships have been found to exist for toluene (Figure 5) and for turpentine (Figure 6). Figure 7, where the variation of the dielectric constant of rubber swollen in bromobenzene, turpentine and toluene is drawn to an arbitrary scale, confirms our previous conclusions. The incorporation of plasticizers leads always to a displacement of the maximum of tan δ toward lower temperatures; in all cases a uniform system is obtained, and the incorporated substance causes

changes in the orientation conditions of all the dipoles. The rate of relaxation does not depend on the nature of the bonds between the dipoles.

The incorporation of plasticizers affects the position of the maximum of tan δ in very much the same way as the introduction of sulfur (see Figure 8 plotted on the basis of data recorded by Scott, Curtis and McPherson[2]) except that, in the latter case, the maximum is shifted towards higher temperatures. The time-constant of the system as a whole changes by the incorporation of sulfur just as by the introduction of a plasticizer.

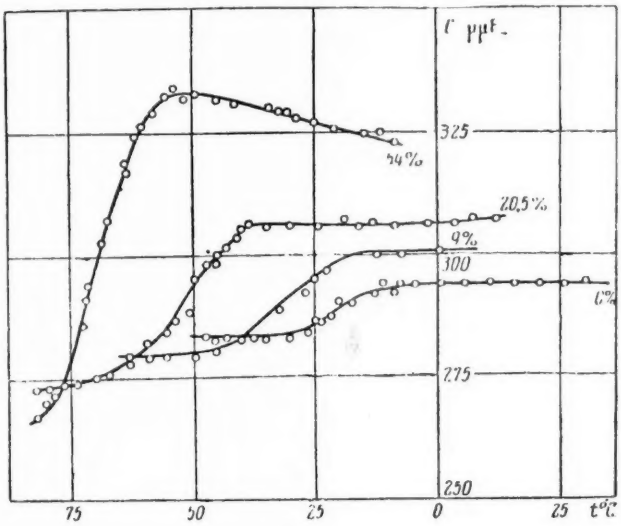

FIG. 7.

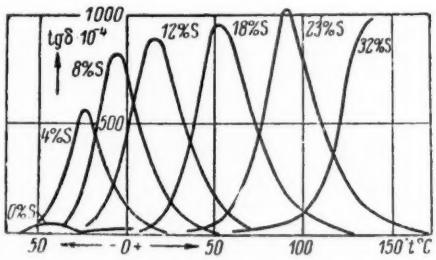

FIG. 8.

The same effect is produced by the introduction of other substances, for instance, rosin.

The modulus of high elasticity and the strength always decrease on incorporation of plasticizers, which indicates a weakening of the bonds in the system. Rosin and combined sulfur behave in a different way, causing an increase of the high elasticity modulus and of the strength. A similar effect is due to an increasing degree of polymerization.

With the increase or decrease of the total energy of the bonds in the system, the rate of relaxation in the system as a whole also increases or decreases. In

the case of non-uniform swelling, the rate of relaxation in any part of the specimen should depend on the degree of swelling.

The results of our experiments show convincingly that rubber and swollen rubber form a uniform system with regard to polarization processes.

This shows that, just as in the case of amorphous substances, in rubbers and analogous polymers, the rate of relaxation of electric processes can be altered by the introduction of foreign substances, forming with them a uniform system.

However, contrary to the case of amorphous substances, a very high macroscopical viscosity perseveres, attaining as much as 10^{16} poises.

With the introduction of nonpolar plasticizers, the absolute value of the dielectric losses decreases, and the maximum of tan δ becomes displaced. This fact might prove useful for the development of elastic dielectrics with low losses.

CONCLUSIONS

1. The maximum of tan δ in rubber and the range of ε-bending are displaced towards lower temperatures when plasticizers are incorporated.

2. The system: rubber—nonpolar plasticizer possesses the same time-constant, which indicates that the plasticizer affects the whole system and not only a definite part of it.

3. The system: rubber—polar plasticizer possesses the same time-constant, which indicates that one and the same activation energy U is required for orientation of the dipoles, regardless whether they are tied together by chemical bonds or by van der Waals forces.

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THE EFFECT OF RAPID STIRRING ON LATEX AND ON ITS CREAMING

J. W. Van Dalfsen

In Table I, on page 317 of the April 1941 issue of Rubber Chemistry and Technology, the expression "Total sulfur" appears twice. In each case, this should have read "Total solids".

COLOR MEASUREMENTS OF LATICES AND OF RUBBER FILMS PREPARED FROM THEM *

G. VAN NEDERVEEN

RUBBER STICHTING, DELFT, HOLLAND

INTRODUCTION

When the *Hevea brasiliensis* tree is tapped, latex flows from the cut as a white or cream-colored liquid, the tone of which varies considerably; in fact some trees have been found to give latex of a pronounced yellow color[4]. The cream color of fresh latex and the yellowish color of standard crepe prepared from such latex is, according to Frey-Wyssling[2], to be explained by the presence of a yellow substance in solution in the resin globules described by this investigator. This colored substance was identified as carotene by Eaton and Fullerton[3].

It is possible, by precoagulation[4], to remove a considerable part of this coloring matter. Its removal is, for example, important in the preparation of sole crepe[5]. Furthermore it is possible, by certain methods of concentrating, such as centrifuging and creaming, to remove a considerable part of the coloring matter with the underlatex. This can also be accomplished by dialysis and clarification[7].

When latex is shipped in preserved form for direct use in the manufacture of rubber products, it is in many cases extremely important that its color be as nearly white as possible. The color of preserved latex is usually darker than that of natural untreated latex, because colored substances are formed during transportation by the action of the iron or tin of the containers. Preserved latex may be bluish gray, yellow or a combination of these colors.

Rhodes and Sekar[8] believe that a bluish gray color is the result of attack of sulfurized proteins in the latex on the iron, whereby ferrous sulfide is formed in a finely dispersed state in the latex. Cotton[9] is of the opinion that a yellow discoloration is the result of oxidation of the ferrous sulfide, in alkaline medium, to ferric hydroxide, which likewise remains in suspension. A mixed color might result from partial oxidation, which would depend on the quantity of oxygen which controls the reduction-oxidation potential of the system. According to Rhodes and Sekar, a dark color is frequently associated with a disagreeable odor, abundant sediment, and low stability.

It is of great importance, therefore, in the control of the quality of latex as a raw material in the direct manufacture of rubber articles, to know how to judge its color, and thereby to be able to set limits to the permissible variations in tone. Of course it is important also to determine the relation between the color of latex and the color of films of rubber prepared from it.

In view of this, an investigation of the measurement of the color of latex and of films prepared from latex was undertaken. First of all it was ascertained what general methods are used for measuring the whiteness of various products like sugar, flour, paper, etc., and, at the same time, what methods have already been proposed for measuring the color of latex.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 17, No. 1, pages 7-9, January 1941; No. 2, pages 23-26, February 1941.

The blancometer of Hilger seemed to be a thoroughly satisfactory instrument for such measurements, and since this instrument was available for the purpose, a study was made of its adaptability.

METHODS FOR DETERMINING COLOR TONES

The color of opaque latex is determined by the nature and quantity of light which is reflected by the surface of the liquid. Accordingly, all methods which are suitable for measuring the colors of solid bodies are, fundamentally, of possible utility for latex. Since latex is ordinarily very pale in color, it was natural to choose those methods which are used for other pale colored products. These methods will be reviewed in a brief way.

It is possible with many pieces of apparatus now known[10], and in common use technically, to express the color of a sample in numerical terms by comparison with an accurately standardized color scale. In this comparative method of judging colors, the colors obtained by blending various proportions of two primary colors are arranged and numbered in a uniform transition series of colors on the scale which corresponds to that of the sample. By comparing a sample with this scale, one estimates by eye the color on the scale which corresponds to that of the sample. In this way the color under investigation can be expressed as a number on the scale.

Instead of comparing the sample with a scale of colors on which color tones are arranaged visibly in series, a series of small colored glasses can be placed on top of one another, and the color in question synthesized and duplicated in this manner. The light which is reflected by a strictly white surface is then colored the same tone as that shown by the sample. The Lovibond colorimeter is a representative means of determining the color of a sample by the method just described.

Color estimation by eye is necessarily subjective, and is difficult to carry out, particularly when differences in white or pale colors are small, as is the case with latex. As will be shown later, the results obtained in measuring the color tones of latex and films prepared from latex by the Lovibond colorimeter were unsatisfactory.

In some industries, such as the flour industry and sugar industry, there is a great need for an accurate method of measuring whiteness, so that the quality of a product can be judged. This need has been felt in recent times also by the textile and paper industries, among other reasons, for controlling the effects of washing and bleaching processes on the color tones of materials which are practically white.

In the beginning, apparatus such as comparison scales, colorimeters, photometers, etc. were used in these determinations, all of which are based on the subjective comparison of the color tone of a sample with a color standard. However, it was impossible to obtain satisfactory results by this method. In the last few years apparatus equipped with photoelectric cells has become common in these industries. Apparatus of this kind depends on a comparison of the light energy of a definite color which is reflected by the sample.

By this means it has been found possible to express barely perceptible differences between white and pale colors in numerical terms, which are at the same time reproducible. In addition to the advantage of relatively great sensitivity, the fact should be stressed that, in using photoelectric cells, the results do not depend on the physiological characteristics of the human eye, and any color estimates are objective. A few types of apparatus, equipped in this way with

photoelectric cells, are described in the technical literature. Mukhin and Kurttz[11], for instance, described an apparatus in which light from an 8-volt lamp was intercepted, after reflection from the surface of the material under examination, by a photoelectric cell, which was connected with a mirror galvanometer. Buehring[12] designed an apparatus in which measurements were made by means of a photoelectric cell in which a current was excited and was then measured by means of a sensitive galvanometer. Magnesium oxide was used as standard for a white surface. Results obtained with this apparatus and with an Ostwald Universal photometer, with samples of white table linen were compared. The results which were obtained with the photoelectric cell ran parallel in all cases with those obtained by simple visual examination; on the other hand, those obtained by the photometer showed notable differences.

An apparatus for determining the whiteness of sugar has been described by Keane and Brice[13], in which the light reflected by the sample and by the standard white surface is intercepted by two separate photocells. The advantage in using two similar photocells lies in the fact that the standard white and the sample do not have to be removed each time, as is the case in the earlier types of apparatus. On the other hand, deviations of the photocells with respect to one another are not detected at once, so there is danger of obtaining erroneous results.

According to a recent publication[14], the effects of various fillers on the colors of rubber articles can be estimated with the apparatus of Higgens[15]. A Steele reflectometer[16] has been used for the same purpose[17].

Finally Lange[18] has placed on the market a photoelectric reflectometer, and Zeiss[19] a leucometer, which are recommended likewise for measuring the whiteness of fabrics, paper, and the like.

A detailed series of tests with the blancometer[20] as a means of determining the whiteness of different kinds of paper has been published by Edge[21]. In his paper Edge mentioned other colors for which the blancometer was found to be useful. At the same time, he reported results which he obtained in measurements of the whiteness of different papers which had been prepared from the same bleached sulfite cellulose, but which, in addition, had been bleached themselves to different degrees. The precision of the results obtained with the same samples of paper, but measured on different days, was stated to be 0.5 per cent of the average readings.

As far as is known to the present author, none of the various types of apparatus just mentioned, with the exception of the blancometer, has ever been used for measuring the color of latex.

LATEX

In the literature of rubber there are a few references to the measurement of the color of latex. Murphy[22], for instance, used a disc method for comparing colors, which is based on visual observation. In this instrument, the sample of latex is compared by direct observation with a yellow or gray standard color, so that it is possible only to determine whether the particular latex does or does not conform to the prescribed standards. Davey[23] prepared a color scale from a mixture of titanium dioxide, lamp black and cadmium sulfide, which was standardized by a Lovibond colorimeter. As with the disc of Murphy, it is possible with the Davey scale to make rapid, though only approximate estimations.

Cotton[24] constructed an apparatus which likewise is based on visual estimation, and which has the advantages of simplicity and low cost. This apparatus consists

of a glass dish which holds the sample of latex, and can be moved with respect to a standard white wall. Horizontal incident light from a standardized light source is reflected by the latex in such a way that it has to pass the front wall of the dish containing the sample twice before it is absorbed in a collimator. Light from the same source is reflected in the same way by a standard white wall, which is so arranged with respect to the source of light and the collimator that both the incident light and reflected light must pass the extended front wall of the dish before it is absorbed by the collimator.

Since the ratio of the whiteness of the latex to the whiteness of the standard is the same as the ratio of the square of the distance of the lamp from the latex to its distance from the standard white, this distance serves as a measure of the whiteness of the latex. Color filters at the end of the collimator make it possible to determine the color tone of a latex both in white light and in lights of the colors of the filters.

The results obtained by Cotton are not very satisfactory. The entire scale, which extended from latex of excellent color to latex of very poor color, covered the range between 40 and 35 cm. distance from the lamp to the latex. The mean error of an individual observer, in an examination of latex without the use of color filtrates, was 0.78 cm.; with an orange filter it was 0.52 cm.; with a blue filter it was 0.38 cm. Different observers obtain values which differ to a still greater extent.

Willott[25] compared color measurements of latex by the Lovibond colorimeter, by the Donaldson colorimeter, and by the Hilger blancometer. Based on the results obtained by these three instruments, the Hilger blancometer or apparatus of similar type was considered to be the best.

Although the methods employed by Murphy, by Davey, and by Cotton have the advantage of simplicity and economy of construction of apparatus, the results obtained by these three methods do not lend encouragement to their use for measuring the color of latex. On the other hand, the experiments which are described below show clearly that promising results, such as obtained by Willott[25] with a Hilger blancometer, can be obtained with this instrument.

MEASUREMENTS WITH THE LOVIBOND COLORIMETER

In the Lovibond colorimeter, the light reflected by the sample is visible in one longitudinal half of a tube, and the light reflected from a standard white surface is visible in the other half of the same tube. The two halves are separated by a longitudinal partition. By inserting colored standard glasses in the second half of the tube, the white light is colored to the point where, judged by eye, it is of the same color as that of the light reflected by the sample. It is preferable to place the sample and standard white surface in diffused or dull light. The standard glasses are numbered so that the color in question can be expressed in Lovibond units.

The results shown in Table I were obtained in an examination, by a Lovibond colorimeter, of five latex films composed of 100 parts of rubber and 5 parts of titanium dioxide. As a basis of comparison, the results obtained with a Hilger blancometer and by eye are shown in the same table.

Compared with the values obtained by the Hilger blancometer and by visual observation, the values obtained by the Lovibond colorimeter, expressed in Lovibond units, show only small and irregular differences. This means, without much question, that the Lovibond colorimeter must be regarded as practically useless for estimating small differences in the color tones of latices.

MEASUREMENTS BY THE BLANCOMETER

The literature which has been cited makes it evident that, in recent years, various types of apparatus, for example, the Hilger blancometer, which depend on the property of photocells to transform impinging light energy into electric energy, have been used with success. It was therefore logical, in trying to judge the color tones of various samples of latex, to make measurements with a Hilger

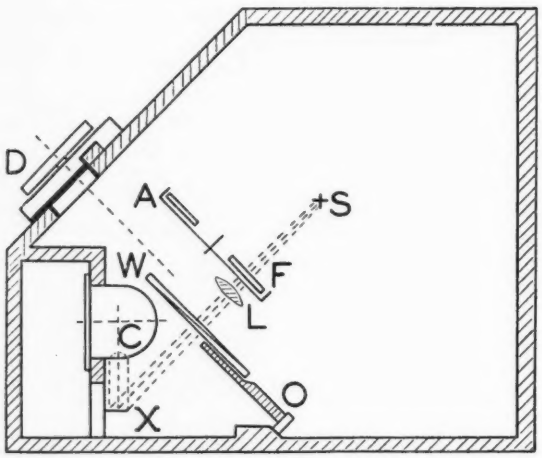

FIG. 1.—Diagram of the path of the beam of light in the blancometer.

S = standard lamp.
A-F = color filter.
L = lens.
W = optical prisms.
X = adjustable sample and standard-white carrier.
C = photocell.
D = screw for adjusting prisms.

TABLE I

COLOR MEASUREMENTS OF LATEX FILMS BY MEANS OF A LOVIBOND COLORIMETER

Sample No.	Color	Series No.	Lovibond units	White light reflection (percentage by blancometer)	Color judged by eye
1.	Brown	52	1.5	57.2	Cream-yellow
	Red	200	0.2		
2.	Red-brown	50	2.0	49.4	Brown
	Green	510	0.1		
3.	Red-brown	50	2.0	42.5	Gray
	Blue	1180	0.4		
4.	Red-brown	50	3.0	34.5	Very gray
	Blue	1180	1.0		
5.	Red-brown	50	2.0	52.3	Brown
	Red	200	0.01		

blancometer, which fortunately was kindly made available by the Rijksvezeldienst (Royal Netherlands Institute for Fibre Research)[26].

The blancometer, the construction of which and path of light in which are shown diagrammatically in Figure 1, consists of a standard electric lamp S, a pair of optical double prisms W, an adjustable holder X for the sample and

for the standard white, and a photoelectric cell C. The standard lamp is maintained at all times at the same, correct light intensity by regulating the applied potential. A light beam from this lamp is centered by lens L, and is then allowed to fall either on the sample under examination or on the standard white, for which magnesium oxide is always used. After being reflected, this beam of light is intercepted by the photoelectric cell. The latter converts the light energy into a weak electric current, the strength of which is measured by a sensitive galvanometer. The deflection of the galvanometer needle is magnified by a microscope, and is observed on a ground-glass plate. The standard white and the sample are fastened on a movable carriage, and can be placed, one after the other, in the path of the same beam of light. The light which falls on the sample is reduced by a set of fixed, dark-glass prisms and, after being reflected, is intercepted by the photocell. The light which falls on the standard white surface is reduced by adjustable prisms of the same kind of dark glass, and is then intercepted in the same way by the photocell.

In this way, by moving the adjustable prisms relative to one another, the light which falls on the standard white can be reduced to the point at which the light energy which it imparts to the photocell is quantitatively the same as that which passes through the fixed prisms and is reflected by the sample. The prisms are moved with respect to one another by means of a worm-gear D. The number of revolutions which the gear makes is indicated by a recording device.

By means of color filters, A-F, which can be inserted between the lamp and the reflecting surface, the reflection, not only of white light, but also of blue green or red light can be measured. The particular blancometer which was used was constructed for measuring the colors of fabrics, paper, and transparent liquids and, therefore, not for measuring the color of an opaque liquid such as latex. This shortcoming is overcome by replacing the regular sample holder by a holder to which a glass dish about 4 cm. in diameter and 1 cm. high can be fastened. This dish is filled with latex to a height so that the surface of the liquid is at the same level as that of the surface of the plate carrying the standard white.

Before any actual measurement is made, a determination is made of the so-called zero position which the adjustable prisms occupy with respect to one another when light from the standard white passes through these prisms and causes the same deflection of the galvanometer as the same light does after passing through the fixed prisms. This zero position is determined by replacing the sample on the movable carrier by a second standard white plate, so that light which is reflected by a standard white surface then passes through both the fixed and movable prisms. The latter are then so adjusted that the galvanometer shows the same deflection in each case. This zero position of the prisms is read on a recording device on the worm wheel. In this position, the same amount of light is absorbed by the fixed prisms as by the movable prisms. The absolute quantity of this light is controlled by the nature of the glass of which the prisms are made.

When the zero position is known, the second plate of standard white is replaced by the sample to be examined. The light reflected by the standard white is then reduced by changing the position of the movable prisms so that the galvanometer shows the same deflection as that shown when the light is reflected on the surface of the sample and is then passed through the fixed prisms. The displacement of the movable prisms is read on the recording device on the worm wheel. This displacement indicates how much energy from the

particular radiation is absorbed by the prisms. This is a measure of the light intensity reflected by the sample.

The factors used in the calculations are as follows:

α = zero position of the movable prisms
β = position of the movable prisms when the samples and standard white are compared
γ = prism constant
I_0 = light intensity after reflection by the standard white and passage through the fixed prisms
I_s = light intensity after reflection by the standard white and passage through the fixed prisms
I_t = light intensity after reflection by the sample and passage through the fixed prisms

As has already been mentioned, when the color of a sample is to be measured, the movable prisms are always so adjusted that:

$$I_s = I_t$$

In the absorption of light by optical prisms the thickness of which is x, the relation:

$$I_x = I_a \cdot {}^{-c_1 x}$$

holds true, in which:

I_a = the intensity of light entering the prism
e = the base of Napierian logarithms
c_1 = a constant characteristic of the material

or, for Briggs' logarithms:

$$I_x = I_a \cdot e^{-c_2 x}$$

in which c_2 is a constant characteristic of the material.

In the case of Hilger blancometer prisms, this equation becomes:

$$I_t = I_0 \cdot 10^{-y(\beta-\alpha)}$$

When expressed as percentage of the standard white, the light intensity (whiteness) of the sample is:

$$W = \frac{100\, I_t}{I_0} = 100 \times 10^{-y(\beta-\alpha)} = 10^{2-y(\beta-\alpha)}$$

in which case:

$$log\ W = 2\text{-}y(\beta\text{-}\alpha)$$

In these relations, y is a known constant which has been determined once for all; β and α are determined for each experiment, and from these W can be calculated.

RESULTS

With the blancometer which has been described, and which is of a form adapted to measurements of latex, the reflections of various latices irradiated with white light and with blue light were determined[27]. Likewise the color of a film of rubber approximately 3 mm. thick, which was prepared by drying a mixture of

these various latices containing 5 parts of dispersed titanium dioxide per 100 parts of rubber and thickened by Latekoll was determined. The results obtained with the various latices and films are summarized in Table II and Figure 2, which

TABLE II

COLORS OF LATICES AND OF FILMS CONTAINING TITANIUM DIOXIDE MEASURED BY THE BLANCOMETER IN COMPARISON WITH THE SAME COLORS ESTIMATED BY EYE

Sample	Latices, percentage reflection		Estimation by eye	Films, percentage reflection in white light
	White light	Blue light		
A	85.0	79.5	Cream	62.0
B	85.0	79.0	Cream	63.6
C	82.5	81.6	Whitish	64.0
D	83.0	78.3	Cream	62.3
E	81.9	77.2	Whitish	60.6
F	82.6	77.6	Whitish	63.5
G	82.6	81.3	Whitish	60.4
H	81.3	75.3	Cream	60.1
I	80.2	75.5	Whitish	61.8
J	81.3	79.0	Grayish	59.7
K	80.6	79.0	Grayish	60.2
L	80.0	77.5	Whitish	60.2
M	79.5	70.9	Cream-yellow	57.4
N	79.1	70.0	Yellow	61.8
O	75.2	65.6	Yellow	39.5
P	78.5	75.1	Gray	60.3
Q	79.7	78.4	Grayish	58.2
R	77.2	75.7	Gray	59.4
S	69.1	69.0	Very gray	55.4
RESIDUAL SAMPLES REMAINING IN THEIR CONTAINERS				
A′	81.9	74.8	Cream	58.8
F′	76.4	74.6	Light cream	54.8
J′	73.4	71.9	Gray	52.3
Q′	62.6	64.5	Gray to black	37.9

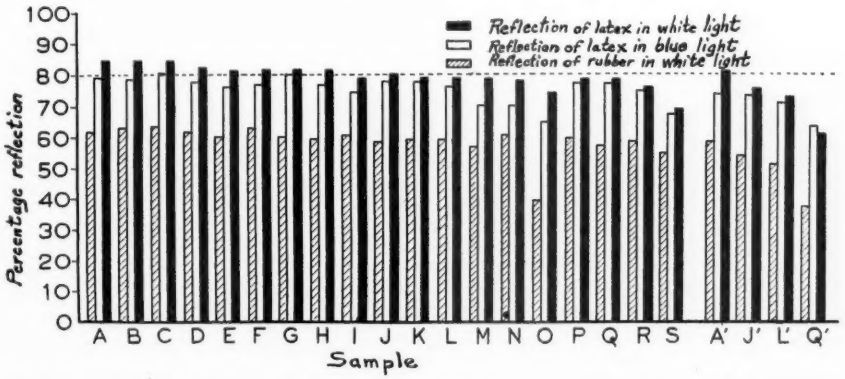

FIG. 2.—Graphical representation of the results of color measurements, by means of a blancometer, of samples of latex and of films of rubber prepared from the latices.

include also the colors of the latices, estimated visually. The reflections of white light by latex, and by the rubber-titanium dioxide films obtained from the latices, are shown separately in Figure 3. The samples of latex which were examined

were from different sources and of different ages, and consequently their colors differed considerably. Samples J, K and L were several years old when examined. In the case of four of the samples, the last two to three liters in the iron containers in which the latices were shipped were kept separate, and their colors determined. These residues contained considerable sediment, and in many cases were darker in color than the rest of the liquid in the containers, provided naturally that the containers had not been shaken too much or that the latex had not been stirred too vigorously.

One of these samples (A′) was of latex from the bottom of an iron container, the inner walls of which were protected by lacquer against attack by the ammoniated latex. The effect of this protective layer of lacquer is evident by the results obtained with white light and blue light.

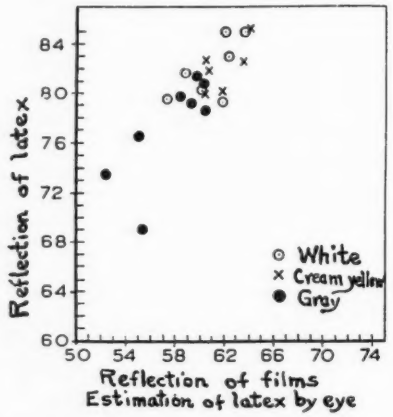

Fig. 3.—Relation between the reflections of latices in white light and of films, prepared from them, containing titanium dioxide.

The results shown in Table II and Figure 2 lead to the following conclusions:

(1) Latices of good color give values for white light and for blue light which are approximately the same, and which, in the case of white light, are 80 per cent or higher.

(2) Latices of yellow color give values for blue light which are considerably lower than those for white light.

(3) Latices of blue-gray color give values for blue light and white light which are approximately the same, but are lower than the corresponding values for white latices.

(4) A comparison of the values, shown in Figure 3, which were obtained with white light—on the one hand with latices, and on the other hand with films containing 5 parts of titanium dioxide per 100 parts of rubber—show that there is a close relationship between the reflection of latex and the reflection of the corresponding films. The small number of points do not, however, make it possible to determine this relation on a quantitative basis. With white latices, the highest values were obtained with white light, both for the latices themselves and for films prepared from them. The reflection of yellow latices is virtually as high as that of white latices, but the reflection of films prepared from yellow latices is lower than that of films prepared from white latices. Finally gray colored latices, and especially films prepared from gray latices, give considerably lower values.

The readings of the position of the movable prisms of the Hilger blancometer in determining the color of latex are given to one decimal place, with a precision of ± 0.2. The values of the reflections of rubber films in white light differ considerably for different positions of the same films and for different films prepared from the same latex, because in this case the method of preparing the films makes itself felt. The mean error in measuring the reflection of white light in five different positions with four identical films was 0.4 per cent, so the W value for these films, with a mean value of 56.3 per cent, was 56.3 ± 0.4. Accordingly, when the values of two latices differ more than 0.4 per cent, or the values of two films differ more than 0.8 per cent, it may be concluded that the two latices are different in color.

SUMMARY

In the introduction to the present work, reasons for latex becoming discolored are reviewed, and the importance of color measurements are discussed. In addition, methods which have been developed for measuring the colors of various socalled white products, such as sugar, flour, paper, and the like, and methods for measuring the color of latex, are reviewed. Some of these methods are subjective; on the contrary, others utilize photocells so that subjective observations are eliminated.

Measurements of the colors of different samples of latices were carried out with a Lovibond colorimeter, as a result of which it was found that this instrument is wholly unsuitable for this purpose.

Measurements of the colors of both latices and films prepared from these latices were then made with a Hilger blancometer. The method of measuring and of calculating the intensity of the reflected light of a definite color is explained.

The results obtained in measurements of the reflection of white light and of blue light from different samples of latex, using a Hilger blancometer, are compared with the results obtained with the same samples of latex estimated by simple visual examination. It was found that latices of good color reflect 80 or more per cent of white light and 78 or more per cent of blue light. The reflection of a yellow latex is considerably less in blue light than in white light. The reflection of a gray latex in white light does not differ much from that in blue light; in each case it is less than 80 per cent.

It is proved conclusively that, judged by measurements of the colors of films, there is a close relationship between the color of a latex and the color of white-pigmented films made from the particular latex.

ACKNOWLEDGMENT

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[26] The present author feels it his pleasant duty to thank A. ten Bruggencate, Director of the Rijksvezeldienst, for his willingness to place the apparatus at our disposal, and R. Smit, of the same Institute, for his collaboration.
[27] The color filters which were used did not make it possible to correlate the measured reflections with the values of an international scale, as have been worked out by the International Lighting Commission (*Trans. Optical Soc.* **33**, 73 (1931-2), and by Hardy and Genossen ("Handbook of Colorimetry"), Cambridge, Mass., **1936**). According to Willott,[25] a modified form of the blancometer is now available, which will make this possible.

THE PROTEINS OF HEVEA BRASILIENSIS

II. ANALYSIS OF A PRODUCT ISOLATED FROM CREPE RUBBER *

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It has long been suspected that proteins played some part in the chemistry and technology of latex and raw rubber, but it is only recently that evidence has been obtained as to their exact function. It is now known,[1, 2] that the proteins in latex are the controlling factors in its stability. Thus, the coagulation point of latex corresponds to the isoelectric point of the proteins in solution; dialyzed latex is not readily coagulated by acid unless a small concentration of salt is added, a property which is also common to the proteins. When latex is concentrated in the factory by centrifugal methods, it is rendered much more unstable, presumably because it has lost a large amount of the protein, which acted as a stabilizing agent.

Knowledge of the influence of proteins on the properties of raw rubber has been much more vague. It is known[3], however, that they do exert a considerable influence on the vulcanizing properties of rubber, and that the water absorption of raw rubber depends on the amount of protein present[4]. More recently Bloomfield and Farmer[5] have shown that, when crepe rubber is fractionated, a series of nitrogen-free fractions are obtained, which are soluble in the usual rubber solvents. The end-fraction, which contains the bulk of the nitrogen, is, however, insoluble. If, however, nitrogen-free rubber (prepared from trypsin-digested latex) is used as the starting material, then all the fractions are soluble. Gee and Treloar[6], using the fractions of Bloomfield and Farmer, have shown that the nitrogen-free fractions fall into a definite molecular series, whereas the fractions which contain nitrogen are radically different in behavior.

Tristram[7] described the isolation and analysis of a protein from dried fresh latex films. It was not known what relationship this product bore to the total protein of latex, or to the protein which is associated with the hydrocarbon in raw rubber. De Vries[8] expressed the opinion that latex contained two proteins, only one of which was precipitated with the rubber, but advanced no evidence to prove this view. Bondy and Freundlich[1] isolated two protein fractions from ammonia-preserved latex, and showed that both had isoelectric points within the precipitation range of latex, but made no statement as to the presence of a third protein. Kemp and Straitiff[2] repeating the work of Bondy and Freundlich[1] claimed the presence of a third protein which was not coagulated with the hydrocarbon. Thus, if the findings of Kemp and Straitiff are correct, latex contains three proteins A, B and C, of which A and B are precipitated with the rubber. The preparation extracted from dried fresh latex films[7] by borate may therefore be a mixture of A, B and C or, more probably, a sample rich in protein C. Unfortunately, none of the above workers characterized his preparation by analytical methods, so that it cannot be said definitely that A, B and C were separate entities. The present work was accordingly carried out to determine the relationship of this borate-extracted protein to the total protein of latex and to the protein found in raw rubber.

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EXPERIMENTAL

The material chosen as the source of protein was the common commercial form, crepe rubber. The method of extraction first tried was that used previously[7], but no protein was isolated. This suggests either that the protein in crepe rubber is somewhat denatured or that the protein is intimately associated with the rubber hydrocarbon. The latter seems to be more probable in view of the findings of Bloomfield and Farmer[5] and of Gee and Treloar[6].

The method of isolation adopted ultimately was based on that of Midgeley, Henne and Renoll[9], since it depended on dissolution of the rubber from the protein. The method has been modified in accordance with recent work in the above laboratories[5].

Method of Isolation

Five hundred grams of shredded crepe rubber were extracted with acetone, in a drip extractor, for 24 hours in an atmosphere of nitrogen. The residue was dried *in vacuo* and then extracted continuously with light petroleum under

Table I

(Results are given as percentage of total nitrogen)

Method	Dried latex 1 Borate buffer	Crepe rubber 2 Organic extraction
Yield	0.1–0.15	0.46
Total nitrogen (ash- and rubber-free)	14.95	14.65
Amide-nitrogen	7.07	7.18
Tyrosine-nitrogen	3.3	3.1
Tryptophan-nitrogen	1.2	0.0–0.7
Arginine-nitrogen	12.9	13.0
Lysine-nitrogen	6.4	6.8
Glutamic acid-nitrogen	7.65	Not less than 1.8
Aspartic acid-nitrogen	6.5	Not less than 4.1

nitrogen in an apparatus designed by Michael[5]. This procedure removed the sol rubber (about 50 per cent of the total), which was virtually nitrogen-free (0.05-0.02 per cent). The remainder, gel rubber, was coagulated with acetone, dried *in vacuo* and exhaustively extracted with xylene at 60-70° C, during which time the mixture was disturbed as little as possible, the organic solvent being replaced by decantation every 24 hours. The residue was next refluxed *in vacuo* with xylene, and the insoluble material removed in the centrifuge. The final residue, a gelatinous mass, was extracted successively with xylene, benzene and toluene, and then dried *in vacuo*. The dry material was brittle and fibrous; it contained 34-35 per cent rubber, 8.13 per cent ash and 8.9 per cent nitrogen; the nitrogen content, ash- and rubber-free, was 14.6 per cent. So far it has not been found possible to separate the protein and rubber otherwise than by methods which involve breakdown of the protein, *i.e.*, acid or alkaline hydrolysis. This finding is in keeping with that of Bloomfield and Farmer[5] discussed above.

Analysis of Product

The yield of protein, after correcting for the rubber content, was 2.3 grams or 0.46 per cent of the crepe. Owing to lack of material the analysis (Table I, 2) could not be made so extensive as those reported previously (Table I, 1), but it was considered that values for ammonia, tyrosine, tryptophan, lysine and

arginine would be sufficient for the purpose of comparison. In addition, the dicarboxylic acids have been investigated qualitatively to test the validity of the claim of Midgeley, Henne and Renoll[9] that glutamic acid is absent from the protein of raw rubber.

DISCUSSION

The results show clearly that the two products have the same contents of ammonia, tyrosine, arginine and lysine and, in view of this agreement, it is suggested that either there is only one protein in latex or that there is a mixture of proteins, of which preparation 1 is a representative sample. The protein from crepe rubber was different in tryptophan content. One sample contained no tryptophan and a second, prepared from a new sample of crepe, contained 0.7 per cent of tryptophan-nitrogen. It is known that tryptophan is a labile amino-acid, being removed from the protein molecule extremely easily by digestion: it is more probable, however, that in the present case some change in the specificity of the amino-acid has occurred in the intact protein molecule during the manufacture of crepe rubber from latex. ($NaHSO_3$ is often added to latex before coagulation with formic acid and, after being coagulated and washed on the rollers, the crepe is dried for 2 to 3 weeks in a tropical atmosphere (30° C ±).) The loss of tryptophan is being investigated and the preliminary results indicate that $NaHSO_3$ does affect this amino-acid. Furthermore, proteinaceous material has been isolated from crepe rubber which had been oxidized in the presence of acetic acid,[10] and it has been found that this material contains only 0.2-0.3 per cent of tryptophan-nitrogen, whereas the tyrosine-nitrogen is 2.8-3.1 per cent. These results suggest that the change in the specificity of tryptophan does take place during the manufacture of crepe rubber.

If the above suggestion is correct, it follows that this protein or mixture of proteins is precipitated, more or less completely, on the coagulation of latex and is thus present in crepe rubber. Such a finding would be in keeping with the evidence of Bondy and Freundlich referred to above[1], but is in contrast to the ideas of de Vries[8] and of Kemp and Straitiff[2]. It has been observed on numerous occasions[11, 12] that some protein does, indeed, remain in the serum after coagulation of the latex. These workers, however, used serum prepared under factory conditions, and it is probable that some of the protein escaped precipitation, since the *p*H would not be rigidly controlled. It is also possible that there is present in latex a small amount of proteinaceous material, probably a degradation product of the native proteins, which remains soluble at the coagulation point of the latex.

That the main bulk of the protein is precipitated is seen from the following experiment. A sample of latex preserved with sodium pentachlorophenate was found to contain 0.136 per cent of protein-nitrogen. The dry rubber content was 38.0 per cent, so that the calculated nitrogen content of the rubber, assuming that the whole of the protein is precipitated, should be 0.37 per cent. A sample of the latex was then coagulated, and the rubber creped under semifactory conditions. The nitrogen content of the crepe was 0.37 per cent.

The analytical results given in Table I are not in complete agreement with the qualitative experiments of Midgeley, Henne and Renoll[9], who obtained no evidence for the presence of cystine, tyrosine and glutamic acid in the proteins of raw rubber. The absence of tyrosine has also been suggested by Kemp and Straitiff[2], who reported that the proteins of latex gave a negative Millon test. It would appear that the analytical methods used by both sets of workers were inadequate for the purpose.

SUMMARY

A protein (2) has been isolated from crepe rubber and analyzed for amide-nitrogen, tyrosine, tryptophan and basic amino-acids. The dicarboxylic acids have been shown to be present.

The results indicate that preparation 2 is of the same composition as preparation 1[7].

It is now suggested that preparation 1 is a representative fraction of the total protein of latex.

Loss of tryptophan has been observed from the protein found in crepe rubber and a reason for this loss has been suggested.

The author wishes to thank Prof. A. C. Chibnall, who was responsible for directing the course of the research, and whose advice and criticism have proved invaluable.

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BUNA FOR HARD RUBBER LININGS *

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The purpose of the investigation described in the present paper was to determine the suitability of artificial or synthetic rubber for hard rubber linings.

Because of the great number of possible variations in compounding, including changes in fillers, softening agents, accelerators and the proportion of natural rubber and artificial rubber, the experiments naturally had to be somewhat restricted in scope. Actually then, the present work describes studies of various types of rubber, including natural rubber, Buna-85, Buna-S, Buna-SS, Perbunan and Perbunan-Extra, in two types of mixtures.

(1) The unloaded mixture:

Rubber	100
Sulfur	25–35
Vulkacit-DM	1.5

(2) The loaded mixture:

Rubber	100
Sulfur	26–28
Vulkacit-576	0–2
Rosin	2
Rard-rubber dust (from natural rubber)	30
Siliceous chalk	30

In some of the experiments, Neoprene was included for comparison.

The unloaded mixture shows more clearly differences between rubbers but, on the other hand, is of only abstract significance, whereas the loaded mixture is of a type adaptable to the development of technical mixtures.

Finally, in tests of chemical stability, several technical mixtures which have proved to be satisfactory as industrial mixtures were included.

Brinell hardness measurements are discussed first; then other mechanical properties, such as processing, chemical stability, permeability to water, and lastly electrical properties.

BRINELL HARDNESS

As a basis for comparing the properties of various types of hard rubber, vulcanizates with as nearly the same hardness values as possible (9.5-10.5) were chosen. As far as most temperature requirements for linings are concerned, this degree of hardness does not seem to be high enough to make the material dangerously brittle and, as far as technical control is concerned, it should be possible to maintain it constant within a wide range of vulcanization.

To determine the relation between Brinell hardness on the one hand and sulfur and accelerator contents on the other hand, the loaded mixture was chosen, and mixtures containing various percentages of sulfur and accelerator were prepared from this base mixture with different types of rubber. Vulcanization was carried out in a press at 150° C for times up to 14 hours.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 16, No. 9, pages 109 116, September 1940.

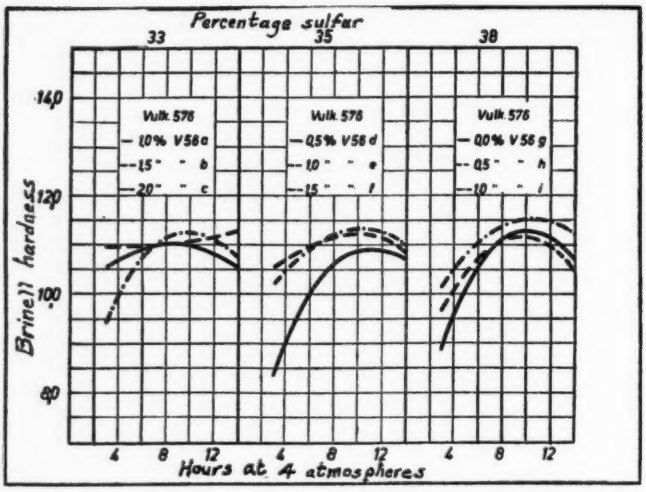

FIG. 1.—Natural rubber.

Mixture: rubber 100, hard-rubber dust 30, rosin 2, siliceous chalk 30.

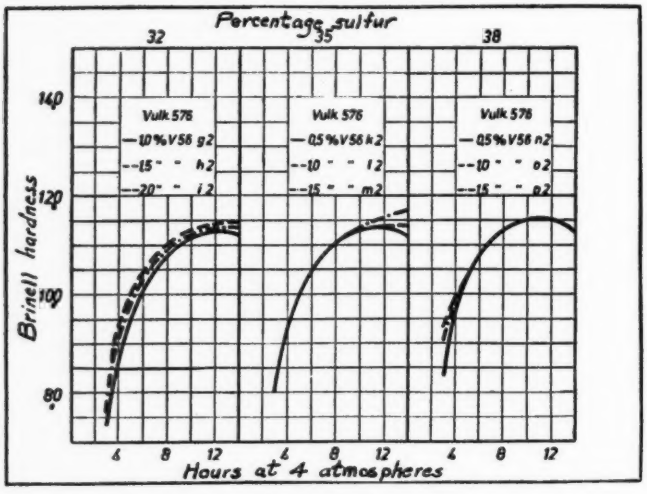

FIG. 2.—Buna-85.

Mixture: Buna-85, hard-rubber dust 30, rosin 2, siliceous chalk 30.

Figures 1 to 6 show that the Brinell hardness depends on the percentage of sulfur, the percentage of accelerator, and the time of vulcanization.

Table I gives in summary form the relation between hardness and percentage of sulfur.

With the relatively low proportions of sulfur used in this series of mixtures, the following conclusions may be drawn.

The Brinell hardness increases with increase in the proportion of vinyl component in the polymer. Of the two vinyl components, *viz.*, acrylonitrile and

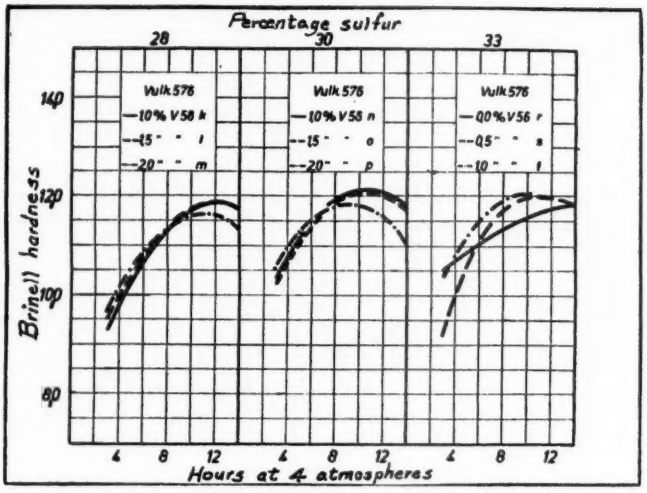

FIG. 3.—Buna-S (Defo 250).

Mixture: Buna-SS 100, hard-rubber dust 30, rosin 2, siliceous chalk 30.

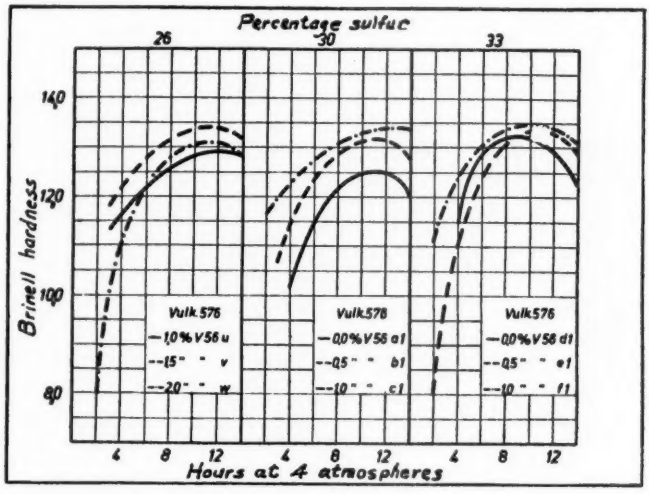

FIG. 4.—Buna-SS (Defo 400).

Mixture: Buna-SS 100, hard-rubber dust 30, rosin 2, siliceous chalk 30.

TABLE I

RELATION BETWEEN BRINELL HARDNESS AND SULFUR CONTENT

Sulfur (percentage)...	26	28	30	33	35	38
Natural rubber.....	—	—	—	11.0–11.3	11.0–11.3	11.2–11.5
Buna-85	—	—	—	11.2–11.4	11.4–11.7	—
Buna-S	—	11.6–11.8	11.8–12.1	11.8–12.1	—	—
Buna-SS	13.0–13.4	13.3–13.6	13.3–13.5	13.3–13.6	—	—
Perbunan	12.5–12.7	12.5–12.8	12.5–12.8	13.0–13.2	—	—
Perbunan-Extra	13.5–13.7	13.6–13.9	13.6–14.0	14.1–14.5	—	—

styrene, the former gives vulcanizates with the higher Brinell hardness values. The curves in Figures 1 to 6 show that, in every case, there is a maximum hardness value which is characteristic of the particular rubber. This increase

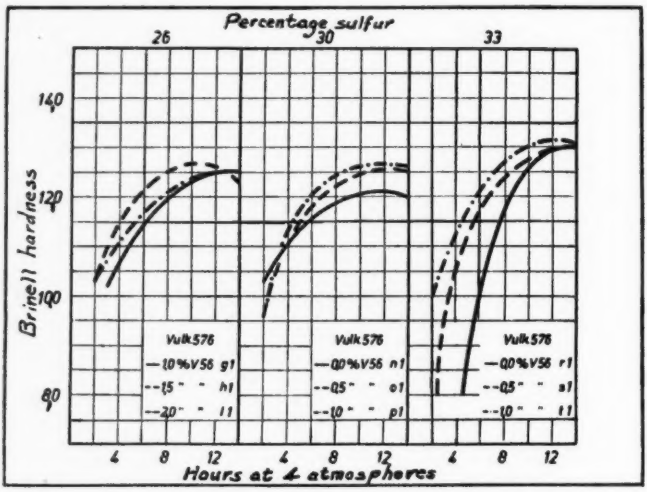

FIG. 5.—Perbunan.
Mixture: Perbunan 100, hard-rubber dust 30, rosin 2, siliceous chalk 30.

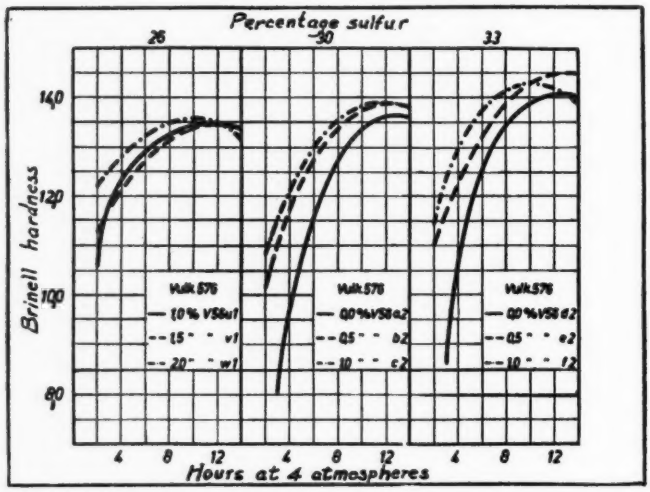

FIG. 6.—Perbunan-Extra.
Mixture: Perbunan-Extra 100, hard-rubber dust 30, rosin 2, siliceous chalk 30.

in hardness to a maximum value with increase in time of vulcanization may be the result of two phenomena. First, combination of sulfur (theoretically too slight to be measured) takes place, with linking of the remaining double bonds

to form cyclized products. After the maximum hardness is reached, continued vulcanization leads to appreciable reversion, which is most pronounced in the case of natural rubber and least so in the case of Perbunan.

MECHANICAL PROPERTIES

To obtain an insight into some of the other properties of hard-rubber vulcanizates prepared from different types of rubber, the vulcanizates containing no fillers and having the same Brinell-hardness values were tested by the usual methods used for hard rubber. With the exception of the test for dynamic bending strength (bending angle), the tests were made with hard rubber test-specimens of normal type ($10 \times 15 \times 120$ mm.). The specimens were vulcanized 30 minutes at 140° C in a press, and then 5 hours in superheated steam at 151° C. The measurements were made three to six days after vulcanization.

To measure the bending angle, a bar ($3 \times 20 \times 140$ mm.), clamped at one end, was subjected to a dynamic bending stress repeated 50 times in a period of approximately 14 seconds, and this treatment was repeated with a greater stress each time. The angle at which rupture occurred was called the bending angle.

The impact resistance (notched-bar test) was measured with normal rods in the same way as in the shock resistance test, except that the flat bar had a saw cut 3 mm. deep on its underside, so that the net cross-sectional area of the bar at this location was 100 sq. mm.

The results of these measurements are shown in Table II.

As already mentioned, the hardness of vulcanizates prepared from mixed polymers increased with increase in the proportion of vinyl component. Consequently if the same hardnesses are desired, the percentage of sulfur must be reduced somewhat.

The Perbunan-Extra vulcanizate showed the highest tensile strength in the particular range of hardness tested.

The greatest heat resistance and the highest bending strength for the particular sulfur contents tested were obtained with Buna-SS and Perbunan-Extra vulcanizates. Perbunan and Perbunan-Extra showed the highest shock resistance. The highest impact strength in the notched-bar test was obtained with Perbunan-Extra.

Measurements of the mechanical properties of vulcanizates prepared from the loaded mixtures, and having a Brinell hardness of 10.5, confirmed the results obtained with the unloaded vulcanizates, although the differences between the various types of rubber were not so clearly defined.

TECHNICAL PROCESSING

Calendering.—Buna-85 mixings tended to blister during calendering and, when the thickness of the sheet was over 1 millimeter, even the addition of stearic acid did not wholly overcome this trouble. Raw slabs of highly plasticized Buna-S (Defo plasticity of 200) and Buna-SS (Defo plasticity of 400-600) were the most satisfactory of all to calender; furthermore, both these rubbers, especially Buna-SS, showed the smallest calender effect.

Tackiness.—Buna-85 mixtures could be plied together very easily by moistening the surfaces with benzine. On the other hand, Buna-S mixtures and Buna-SS mixtures were in most cases rendered tacky only by application of special adhesives, such as a dilute solution of rosin or a solution of rubber containing

TABLE II

MECHANICAL PROPERTIES OF UNLOADED HARD RUBBER MIXTURES

Type of rubber	Sulfur (percentage)	Time of vulcanization (hours)	Brinell hardness (kg. per sq. mm.) After 10 sec.	Brinell hardness (kg. per sq. mm.) After 60 sec.	Tensile strength (kg. per sq. cm.)	Elongation at rupture (mm.)	Martens value (°C)	Static bending strength (kg. per sq. mm.)	Dynamic bending angle	Shock resistance (cm. per kg. per sq. cm.)	Impact resistance (notched-bar test, cm. per kg. per sq. cm.)
Natural rubber	35	3	9.3	9.0	517	3.3	67	627	24	23.5	7
	32	5	9.3	8.8	512	3.0	68	(1049)	(slight)	(84.2)	7.6
Buna-85	38	5	9.1	8.6	500	3.5	62	577	18	4.23	6.2
	35	5	9.0	8.5	458	3.2	65	521	19	15.9	7
Buna-S (Defo plasticity 250)	30	3	9.0	8.5	537	6.5	67	590	24	15.9	7.2
	27	5	9.0	8.5	526	3.8	63	542	22	15.9	6.7
Buna-SS (Defo plasticity 400)	28	3	10.3	10.0	629	3.2	76	662	21	15.9	6.4
	25	3	10.2	9.9	579	3.7	70	622	20	13.9	6.2
Perbunan	26	5	9.6	9.2	614	3.0	60	613	18	37.8	6.4
	24	5	9.4	8.8	593	3.8	59	577	20	37.8	6.7
Perbunan-Extra	26	3	10.5	10.0	665	4.5	73	703	20	42.2	7.2
	24	5	10.3	9.9	657	4.3	74	672	22	26.7	8.2

rosin. Particularly satisfactory results were obtained with solutions prepared with benzine, of the following compositions:

(1) For treating metal:

Buna-SS (Defo plasticity 600)	100
Sulfur	20
Vulkacit-DM	3
Koresin	5
Whiting	20
Zinc oxide (Red Seal)	140

(2) For building plies and for adhering seams:

Buna-SS (Defo plasticity 600)	100
Sulfur	20
Vulkacit-DM	3
Koresin	10

Plasticity and elasticity.—In covering rims, ribs and recesses or cavities, it is necessary that the material be especially pliable. The elastic component of the raw material should be as low as possible, and its extensibility as great as possible. Both these requirements are best fulfilled by highly plasticized Buna-S and Buna-SS; Buna-85 is also satisfactory. Occasionally, in covering an angular, curved plate, surface cracks appear on the edges where the material is laid over an angle of 180°. This is especially evident after vulcanization. Such cracks appear when the lining material is too resilient, has too pronounced a calender effect, has too low an extensibility, and has not been mixed thoroughly. When the lining is too resilient, it lifts off the surface at reëntering angles during vulcanization. This tendency can be minimized by proper compounding or by plasticization.

Stability during storage.—During several years' experience with Buna-S which had been plasticized to a Defo plasticity of 250, it was found that calendered sheets always had to be processed over again. As is well known, the effects of thermal softening become noticeably less during storage; in fact, the elastic component in the mixture increases so greatly after a few weeks that the mixture can no longer be relied upon to process satisfactorily. This change could have been prevented if a stabilizing agent had been available.

In the curves of Figure 7, the influence of the stabilizing agent LS-1 on plasticized Buna-S can be seen. Buna-S was softened thermally to a Defo plasticity of 250, and was then mixed immediately on a mill with various percentages of the stabilizing agent LS-1. As is evident from the course of the curves, the addition of 2 per cent or more of this agent is of considerable value in stabilizing the mixture, especially with respect to the recovery of the elastic component of the plasticized Buna-S. The addition of approximately 1.5 per cent or less tends, on the contrary, to increase the Defo hardness and the elastic component of the mixture.

CHEMICAL STABILITY

The frequent exposure of hard rubber linings to chemicals of the most varied types, with simultaneous exposure to heat, requires a high resistance of the material to these adverse influences. Changes in volume first occur, as a result of swelling, dissolution or chemical attack. These changes can be easily measured, and it is thus possible to predict to a certain degree the serviceability of the material.

Since the change in volume depends primarily on the character of the surface, vulcanized samples were tested both in steam and in hot air, for, during vul-

canization in hot air, partial oxidation of the surface occurs, with the result that the outer layer becomes harder, more brittle and chemically more resistant.

Test-specimens.—Circular pieces, 21 mm. in diameter and 4 mm. thick, served as test-specimens. They were first heated 30 minutes in a press, perforated with a 4-mm. hole so that they could be suspended and, after removal of the frame, were hard-vulcanized either in steam at 150° C for 3 and 5 hours, or in hot air at 150° for 5 and 8 hours. Only in the case of samples prepared from polymerized chlorobutadiene, was it necessary to extend the time of heating to 8 and 13 hours to obtain the desired hardness.

The test-specimens were kept in contact with the substances listed below for 8 weeks; at the end of each week they were removed from the liquid and, after

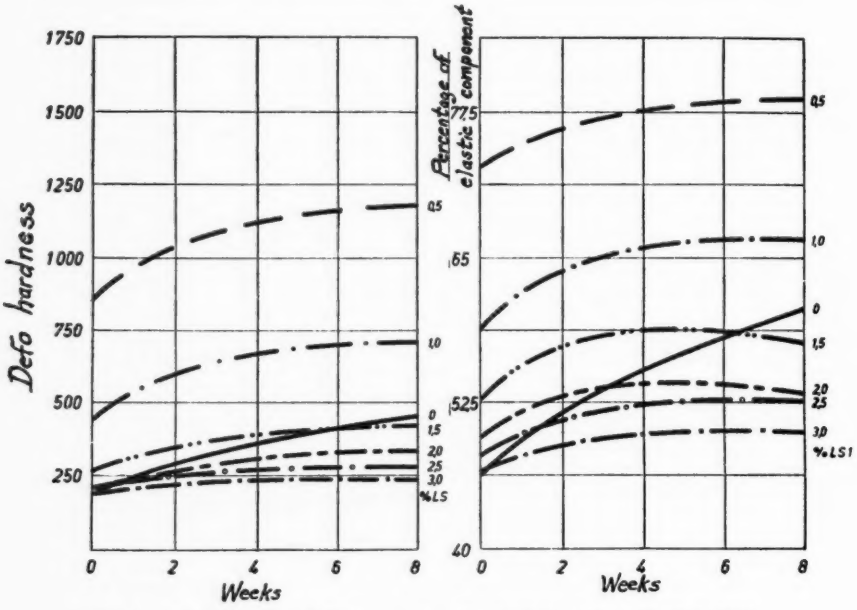

FIG. 7.—Influence of a stabilizing agent on the plasticity of Buna-85 (Defo 250).

being thoroughly brushed, rinsed and dried, were weighed, so that the volume changes could be computed. The mixtures recorded in Table III (among them industrial mixtures Nos. 3, 4, 9, 12 and 17) were tested in this way.

Chemical reagents.—The following chemical conditions were chosen for study:

Water at 95° C.....	8 weeks (Figure 8)
Nitric acid (32%) at 20° C.....	8 weeks (Figure 9)
Chlorine gas at 70–75° C.....	4 weeks (Figure 10)
Chlornatron at 20° C (renewed each week)..	8 weeks (Figure 11)
Benzene at 20° C.....	8 weeks (Figure 12)

Further experiments were carried out with the following substances:

Concentrated hydrochloric acid at 20° C....	12 weeks
Sulfuric acid (15%) at 20° C.....	12 weeks
Concentrated sulfuric acid at 20° C.....	8 weeks
Concentrated hydrofluoric acid at 20° C.....	2 weeks

Results of the tests.—The relatively great capacity of soft Neoprene mixtures to absorb water is already known (see Figure 8). This was found to be true of hard Neoprene vulcanizates as well. All vulcanizates cured in hot air absorbed

TABLE III

COMPOSITIONS OF THE MIXTURES

	Natural rubber			Buna-85			Buna-S		
No.	1	2	3	4	5	6	7	8	9
Rubber (percentage by weight)	75.0	73.3	58.4	49.5	73.3	71.7	77.8	76.0	49.7
Sulfur (percentage on rubber)	32	35	35	45	35	38	27	30	32
Natural rubber	100.0	100.0	100.0	100.0	—	—	—	—	—
Buna-85	—	—	—	—	100.0	100.0	—	—	—
Buna-S (Defo 250)	—	—	—	—	—	—	100.0	100.0	90.0
Plastikator-32	—	—	—	—	—	—	—	—	10.0
Brown-coal tar pitch	—	—	—	30.0	—	—	—	—	—
Mineral oil	—	—	2.7	—	—	—	—	—	—
Hard rubber dust	—	—	32.0	25.0	—	—	—	—	50.0
Siliceous chalk	—	—	—	—	—	—	—	—	15.0
Sulfur	32.0	35.0	35.0	45.0	35.0	38.0	27.0	30.0	32.0
Vulkacit-576	—	—	1.5	2.0	—	—	—	—	1.5
Vulkacit-DM	1.5	1.5	—	—	1.5	1.5	1.5	1.5	—
LS-1	—	—	—	—	—	—	—	—	3.0
	133.5	136.5	171.2	202.0	136.5	139.5	128.5	131.5	201.5

No.	10	11	12	13	14	15	16	17	18
Rubber (percentage by weight)	79.1	77.3	45.4	79.7	78.5	79.7	78.5	41.8	63.5
Sulfur (percentage on rubber)	25	28	45	24	26	24	26	45	35
Natural rubber	—	—	—	—	—	—	—	40.0	—
Buna-115	—	—	—	—	—	—	—	60.0	—
Buna-S (Defo 250)	—	—	90.0	—	—	—	—	—	—
Buna-SS (Defo 400)	100.0	100.0	—	—	—	—	—	—	—
Perbunan	—	—	—	100.0	100.0	—	—	—	—
Perbunan-Extra	—	—	—	—	—	100.0	100.0	—	—
Neoprene	—	—	—	—	—	—	—	—	100.0
Plastikator-32	—	—	10.0	—	—	—	—	—	—
Oppanol-B-200	—	—	50.0	—	—	—	—	—	—
Brown-coal tar pitch	—	—	—	—	—	—	—	30.0	—
Rosin	—	—	—	—	—	—	—	2.0	—
Hard rubber dust	—	—	25.0	—	—	—	—	—	—
Powdered graphite	—	—	—	—	—	—	—	40.0	—
Fumonex	—	—	—	—	—	—	—	20.0	—
Zinc oxide (Red Seal)	—	—	—	—	—	—	—	—	10.0
Light magnesia	—	—	—	—	—	—	—	—	10.0
Sulfur	25.0	28.0	40.0	24.0	26.0	24.0	26.0	45.0	35.0
Vulkacit-576	—	—	—	—	—	—	—	2.0	1.5
Vulkacit-DM	1.5	1.5	1.5	1.5	1.5	1.5	1.5	—	—
LS-1	—	—	3.0	—	—	—	—	—	—
	126.5	129.5	219.5	125.5	127.5	125.5	127.5	239.0	156.5

more water than did the corresponding vulcanizates cured in steam. Buna-85, Buna-S and Buna-SS swelled least in water, and were superior to natural rubber in this respect.

Neoprene was the most resistant product to nitric acid (see Figure 9); the unloaded Buna-SS mixture vulcanized in hot air was the next most resistant product. Perbunan vulcanizates were destroyed most rapidly.

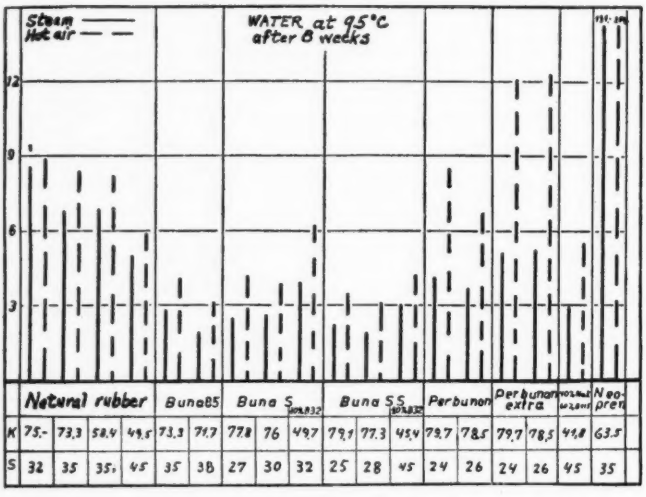

FIG. 8.—Percentage increases in volume of natural rubber and various types of synthetic rubbers in water at 95° C.

K=percentage rubber.
S=percentage sulfur (based on rubber).

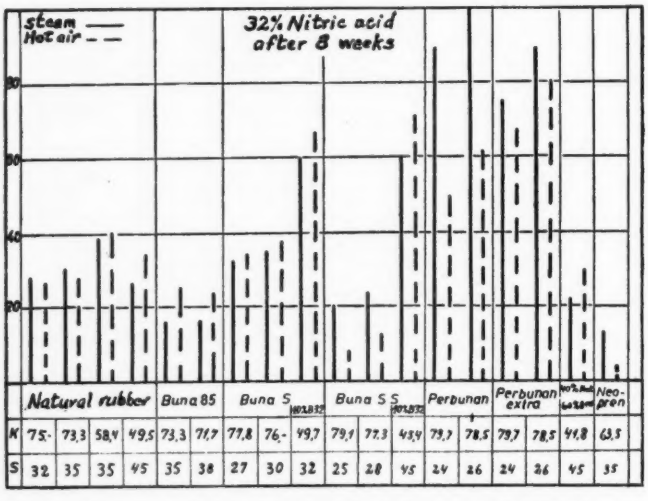

FIG. 9.—Percentage increases in volume of natural rubber and various types of synthetic rubbers in 32% nitric acid.

K=percentage rubber.
S=percentage sulfur (based on rubber).

In chlorine gas, Buna-85 vulcanizates cured in steam showed the smallest decreases in volume; natural rubber products showed similar but greater changes. Perbunan, Perbunan-Extra and Neoprene vulcanizates cured in steam decreased

considerably in volume. In the case of Perbunan vulcanizates, the oxidized outside layer, formed during vulcanization in hot air, was considerably more resistant to chlorine gas than the unoxidized surface of the vulcanizates cured in steam. The Neoprene vulcanizate cured in hot air increased 38 per cent in volume, and was discarded as useless.

In chlornatron, all vulcanizates cured in hot air were more stable than the corresponding vulcanizates cured in steam. The resistance was better with the higher proportions of sulfur and at the higher states of vulcanization (see Figure 11). Neoprene gave poor results.

In benzene, the samples vulcanized in steam and those containing the higher proportions of sulfur swelled least. Perbunan-Extra vulcanized in steam was the best. With all the different types of rubber, improved resistance to benzene

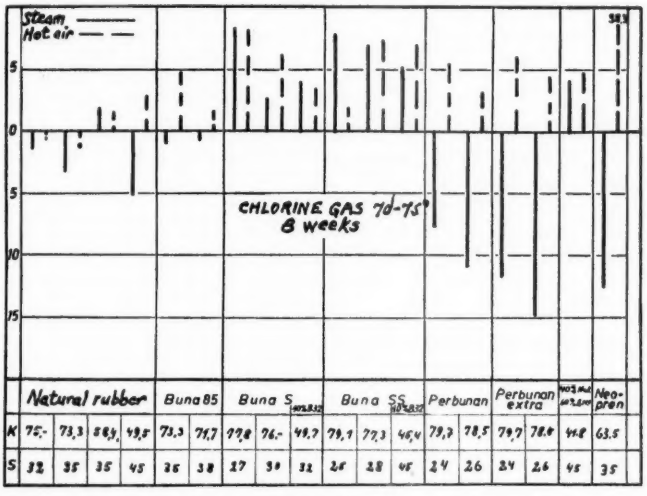

FIG. 10.—Percentage increases in volume of natural rubber and various types of synthetic rubbers in chlorine gas at 70-75° C.

K=percentage rubber.
S=percentage sulfur (based on rubber).

can be obtained by increasing the proportion of sulfur if the intended service allows this in the face of the accompanying disadvantage of poorer mechanical properties. Buna-SS was superior to natural rubber. The other test-specimens ruptured after a few days because of the swelling pressure.

The differences in stability toward hydrochloric acid and toward dilute sulfuric acid were only slight, even after 3 months. As was to be expected, however, the Perbunan vulcanizates, especially those cured in hot air, failed to show good resistance. High proportions of sulfur improved the chemical resistance, but here too at the expense of the mechanical properties.

In concentrated sulfuric acid, all samples carbonized and were destroyed in a few weeks; only a blended mixture (No. 12 prepared from Buna-S and Oppanol (Vistanex)) could be measured after 8 weeks, in which case the increase in volume was 250 per cent.

In hydrofluoric acid, the best results were obtained with a heavily loaded industrial mixture (No. 17), composed of a blend of natural rubber and num-

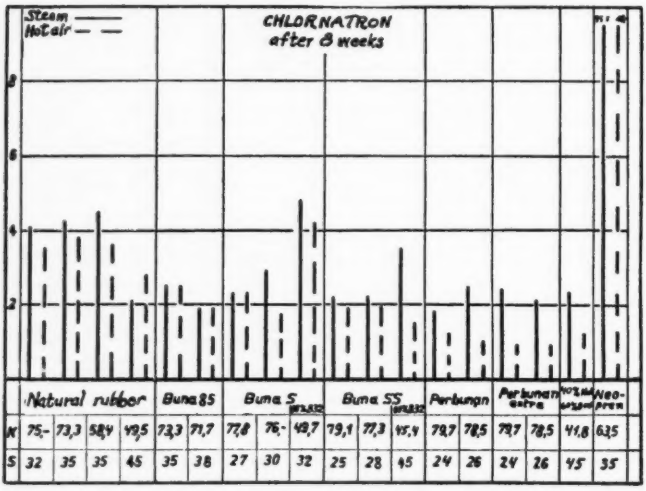

FIG. 11.—Percentage increases in volume of natural rubber and various types of synthetic rubbers in chlornatron.

K=percentage rubber.
S=percentage sulfur (based on rubber).

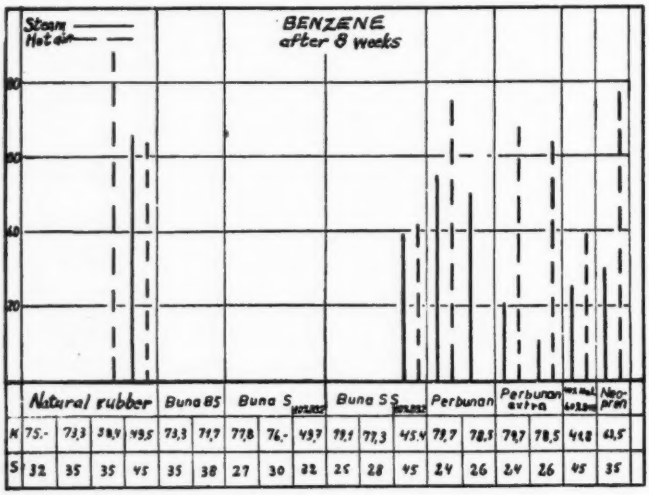

FIG. 12.—Percentage increases in volume of natural rubber and various types of synthetic rubbers in benzene.

K=percentage rubber.
S=percentage sulfur (based on rubber).

bered Buna. Neoprene showed high resistance to hydrofluoric acid, especially the samples vulcanized in steam. Buna-SS was the third best material. All other samples were destroyed within only two weeks.

PERMEABILITY TO WATER VAPOR

The permeability of sheets 0.1 to 0.2 mm. thick and 70 mm. in diameter to water vapor at 20° C was measured in moving air with a relative humidity of 85 per cent.

To lower the permeability to water vapor still further, two Buna-S mixtures containing Oppanol (Vistanex) (Nos. 19 and 20), besides the loaded mixtures shown, were tested for permeability to water. The compositions of the Buna-S-Oppanol (Vistanex) mixtures were as follow:

	No. 19	No. 20
Buna-S (Defo plasticity 600)	100	100
Oppanol-B-200 (Vistanex)	30	30
Sulfur	30	40
Vulkacit-DM	1.5	1.5
LS-1	3	3
	164.5	174.5

TABLE IV

PERMEABILITY TO WATER VAPOR

$$\left(K = \frac{\text{g. cm}}{h.\ (\text{sq. cm.}).\ \text{mm. Hg}} \times 10^{-8}\right)$$

Type of rubber	No. of mixing	Sulfur (percentage based on rubber)	2 hrs./3 atmos. $K \times 10^{-8}$
Natural rubber	1	32	0.3
	2	35	0.3
	3	35	0.3
Buna-85	5	35	0.6
	6	38	0.6
Buna-S	7	27	0.4
	8	30	0.5
	9	32	0.6
Buna-SS	10	25	0.5
	11	28	0.5
Perbunan	13	24	1.0
	14	26	1.1
Perbunan-Extra	15	24	1.0
	16	26	1.0
Buna-S	25	30	0.5
Oppanol (calculated on rubber)	26	40	0.3

As is evident from Table IV, Perbunan and Perbunan-Extra were much more permeable to water vapor than are the other types of rubber, both natural and synthetic. The permeability was reduced when the percentage of sulfur was increased. Addition of Oppanol (Vistanex) to Buna-SS made the latter as impermeable as natural rubber to water vapor.

ELECTRICAL PROPERTIES

To test the electrical properties, unloaded mixtures were vulcanized in the form of sheets 1 mm. thick in a press, and the electrical properties of the sheets were measured in their original state (column (1) in Table V), after they had been aged in an air oven at 100° C for 14 days (column (2) in Table V).

With all vulcanizates, the surface resistance was over 10^7 megohms, which corresponds to a relative value of 12 of the V.D.E. When measured in the original state, the specific resistance of Buna-SS and that of Buna-85 were somewhat higher than that of natural rubber, but after aging in the oven, the specific resistances of all types of rubber increased to values over 10^{16} ohms per cm.

The dielectric constants (*tan* δ, D.K.) show clearly the influence of acrylonitrile in mixed polymers. In the *tan* δ value, Buna-SS surpassed the other types of

TABLE V

ELECTRICAL PROPERTIES

(1000 V)

Rubber	Sulfur (percentage)	No. of mixing *	Ohms per cm. $\times 10^{15}$ (1)	Ohms per cm. $\times 10^{15}$ (2)	tan δ (50 Hertz) (1)	tan δ (50 Hertz) (2)	Dielectric constant (50 Hertz) (1)	Dielectric constant (50 Hertz) (2)
Natural rubber	32	1	8.4	Higher than 10^{16}	0.0056	0.0050	2.9	2.9
Natural rubber	35	2	8.8	Higher than 10^{16}	0.0056	0.0066	2.9	2.9
Buna-85	35	5	10.0	Higher than 10^{16}	0.0076	0.0067	2.9	2.9
Buna-85	38	6	10.0	Higher than 10^{16}	0.0077	0.0078	3.0	3.0
Buna-S (Defo 250)..	27	7	6.8	Higher than 10^{16}	0.0057	0.0050	3.0	3.0
Buna-S (Defo 250)..	30	8	4.7	Higher than 10^{16}	0.0047	0.0051	2.9	2.9
Buna-SS (Defo 400).	25	10	10.0	Higher than 10^{16}	0.0029	0.0035	2.9	2.9
Buna-SS (Defo 400).	28	11	10.0	Higher than 10^{16}	0.0033	0.0045	3.0	3.0
Perbunan	24	13	2.6	Higher than 10^{16}	0.0014	0.0084	4.0	4.0
Perbunan	26	14	5.4	Higher than 10^{16}	0.0096	0.0088	3.9	3.9
Perbunan-Extra	24	15	5.0	Higher than 10^{16}	0.0098	0.0101	4.2	4.2
Perbunan-Extra	26	16	3.2	Higher than 10^{16}	0.0093	0.0114	4.1	4.2

(1) Original state.
(2) After 14 days in air oven at 100° C.
* The compositions are given in Table III.

rubber, a confirmation of the fact that, among soft-vulcanized rubbers, Buna-SS is regarded with special favor among synthetic rubbers as a material for cable insulation.

SUMMARY

On the basis of the investigations described in the present paper, certain rules or directions for obtaining the most desirable properties with the various types of artificial rubbers can be laid down.

Brinell hardness.—The higher the proportion of vinyl component in a mixed butadiene polymer, the harder is the resulting vulcanizate within the relatively narrow range of percentages of sulfur which were tested. In this respect, acrylonitrile has a greater effect than does styrene.

Mechanical properties.—As far as mechanical properties are concerned, Perbunan-Extra is an extraordinarily good material for, in addition to giving high Brinell hardness and tensile strength, it also shows good shock resistance and impact strength. Buna-SS and Perbunan-Extra give, within the range of hardnesses tested, high Martens values. Compared with natural rubber, their resistances to dynamic bending are particularly good.

Processing.—By thermal plasticization with the aid of stabilizing agents, it becomes possible to obtain easily processed hard rubber mixtures from Buna-S. Buna-85, too, can be readily processed, but it is more difficult to calendar without blisters. In plying or doubling sheets and in making seams and joints with Buna-S, good results are obtained with benzine; for the same work with Buna-SS, good results are obtained with dilute solutions of rosin.

CHEMICAL STABILITY

Reagent	Very satisfactory	Unsatisfactory
Water	Buna-85, Buna-S and Buna-SS vulcanized in steam Natural rubber	Neoprene
Hydrochloric acid	Natural rubber Buna-85 Buna-S Buna-SS Natural rubber (all equally good)	Perbunan Perbunan-Extra
Sulfuric acid (dilute)	Natural rubber Buna-85 Buna-S Buna-SS (all equally good)	Perbunan Perbunan-Extra
Hydrofluoric acid	Heavily loaded blends of natural rubber with Zahlenbuna Neoprene Buna-SS	Perbunan Perbunan-Extra
Nitric acid	Neoprene Buna-SS (both vulcanized in hot air)	Perbunan Perbunan-Extra
Chlorine gas	Buna-85 vulcanized in steam Natural rubber	Perbunan Perbunan-Extra (both vulcanized in steam)
Chlornatron	Buna-85 Buna-S Buna-SS Perbunan Perbunan-Extra (in all cases, particularly when containing high percentages of sulfur and vulcanized in hot air)	Neoprene
Benzene	Perbunan-Extra (with high proportions of sulfur)	Natural rubber Buna-85 Buna-S Buna-SS

Types of rubber not included in the table above are of mediocre quality in their resistance to chemicals.

Permeability of water vapor.—Carefully controlled vulcanizing conditions, relatively high percentages of sulfur, and the addition of Oppanol (Vistanex) are contributing factors in minimizing the permeability of hard vulcanizates to water vapor.

Electrical properties.—With respect to insulating properties, natural rubber and Buna-SS are equally good. As semi-conductors, Perbunan and Perbunan-Extra give the poorest results.

THE POLAROGRAPHIC DETERMINATION OF ORGANIC ACCELERATORS OF VULCANIZATION *

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In spite of the great importance which vulcanization accelerators have attained in the rubber industry, there is still an almost complete lack of analytical methods, both for determining the accelerator contents of rubber mixtures and for identifying accelerators in vulcanized rubber. Apart from the wholly unsatisfactory and uncertain method of deciding the existence of organic accelerators in vulcanized rubber by a Kjeldahl nitrogen determination, there is little of value in the literature.

Twiss and Martin[1] have described a few qualitative reactions of accelerators. Recently Shimada[2] described some color reactions of accelerators with cobalt oleate, but the analytical utility of these reactions is very doubtful. Of far more promise than these is the polarographic method, the value of which in the analytical determination of a series of important accelerators was proved in an investigation which will be described in the present paper.

It had already been proved in earlier polarographic investigations that organic compounds containing nitrogen with a double bond can be reduced electrolytically, provided groups with a tendency to rupture are close to the double bond. Shikata and Tachi[4] have shown this to be true of azobenzene, and Winkel and Proske[5] of dimethylquinoxaline.

It seemed likely, therefore, that vulcanization accelerators, which likewise contain double-bonded nitrogen as well as easily ruptured groups, *e.g.*, 2-mercaptobenzothiazole and other important accelerators derived from this, such as benzothiazyl disulfide, are also reducible electrolytically, and hence can be determined by the polarographic method.

The investigation which is described below proved that this is actually true. Not only this, but it also was found that other accelerators with similar polarographically active groups can be determined in the same way, *e.g.*, the important accelerator tetramethylthiuram disulfide, and the piperidine salt of pentamethylenedithiocarbamic acid.

On the other hand, it was found that basic accelerators derived from guanidine, *e.g.*, diphenylguanidine, cannot be determined by the polarographic method.

The fundamental principles of the polarographic method have already been discussed in detail by Winkel and the present author[6], and therefore only a few of its significant features will be pointed out at this time.

THE POLAROGRAPHIC APPARATUS

In the work described in the present paper, a 1938 model polarograph from the firm of E. Leybold's Nachfolger, of Köln-Bayenthal, was used. This polarograph, which is simpler than the earlier ones, and which is designed especially for industrial use, was found to be particularly useful in the present investigation.

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In this apparatus, the electrolytic potential is read by two rotating potentiometers. One of these potentiometers serves to regulate the electrolytic potential at which it is desired to take polarographic photographs to any initial value within the range of -2 to $+2$ volts. The other potentiometer is turned by a motor installed as an integral part of the apparatus, and covers a range of 2 volts, as long as a 4-volt accumulator is connected with the apparatus. In addition, the apparatus has a controller with which the sensitivity of the galvanometer can be controlled within a range of 1:2500 in twenty-two steps. To avoid the inconvenience of having to calibrate the apparatus each time a new capillary is used, a calibration device is added with which it is possible to make the step height of the polarograph any value which is desired. With the electrolysis stand belonging to the apparatus, the disagreeable problem of working with mercury is solved in the best possible way. Spattering of residual mercury is very unlikely, and damage to the fine glass capillary is likewise extremely improbable. To reduce the consumption of mercury to a minimum (only the most highly purified, distilled mercury should be used), a specially constructed electrolysis vessel was used in the investigation described in the present paper. On the bottom of this vessel, which was of approximately 30-cc. capacity, was a layer of mercury, which served as the anode. On the mercury was placed normal potassium chloride solution. In the electrolysis vessel, which was constricted at the top, was suspended a small container carrying the solution under investigation. Passage of the current between this suspended receptacle and the anode liquid took place through a diaphragm cemented into this receptacle. By this means any mixing of the solution under investigation with the anode liquid was avoided. From time to time the potassium chloride solution on the layer of mercury was renewed. It was found possible to use the mercury itself for a long time without change.

PREPARATION OF THE SOLUTIONS TO BE INVESTIGATED

The most important requisite in obtaining reliable polarographic curves which can be evaluated with a fair degree of accuracy is the preparation of a suitable solution. In the present investigation methyl alcohol was found to be the solvent best adapted to the purpose. A few of the accelerators which were insoluble in methyl alcohol were dissolved in a little chloroform, and these solutions were then diluted with methyl alcohol.

According to previous work by Winkel and Proske[7], the electrolytic reducibility of organic compounds depends to a great extent on the hydrogen-ion concentration of the solution under investigation. Reduction takes place most easily in solutions which are strongly acidic; with increasing pH value reduction becomes less and less easy. At a pH of approximately 4, the depolarization potential changes abruptly, *i.e.*, it increases to a much higher value, which then remains almost constant to a pH range of 12-14, providing the substance does not change chemically in the alkaline solution. This interesting phenomenon will not be discussed further in the present paper, for the subject has been dealt with in detail in an earlier publication[7]. In the present investigation, this behavior is of importance, because it seemed advisable from the beginning to carry out the measurements in various ranges of pH, not because the height of the step depends to a great extent on the hydrogen-ion concentration. Hydrogen chloride, potassium chloride, ammonia and sodium hydroxide were used as electrolytes, and these had a determinant influence on the pH values of the solutions.

For further details concerning the compositions of the base solutions used in

studying the various accelerators, the reader is referred to another publication of the author[8].

For accelerators to be examined, the technical grades of the I.G. Farbenindustrie A.-G., were used. They were freed of the crudest impurities by crystallizing them once from chloroform. One-hundredth molar solutions of the accelerators were then prepared (in the case of accelerators of unknown chemical compositions, approximately 0.4 gram of accelerator was dissolved in 100 cc. of solvent), to 10 cc. of each solution was added 40 cc. of the base solution, and the resultant solution was examined polarographically.

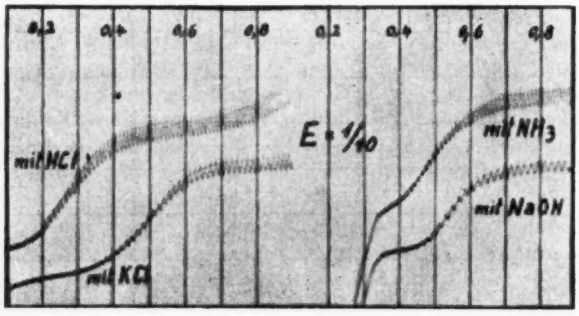

FIG. 1.—Polarograph of 2-mercaptobenzothiazole in acid, neutral and alkaline solutions.

TABLE I

RESULTS OF POLAROGRAPHIC MEASUREMENTS OF ORGANIC VULCANIZATION ACCELERATORS

		HCl		KCl		NH		NaOH	
	Concentration	DP	h	DP	h	DP	h	DP	h
Vulkacit Mercapto...	0.002 molar	0.16	6	0.37	6	0.41	5	0.48	4
Vulkacit-AZ	0.8 g. per liter*.....	0.11	21	0.34	22	0.29	21	0.39	18
		0.62	21	—	—	—	—	—	—
Vulkacit-DM	0.002 molar	0.20	39	0.44	39	0.36	39	0.44	39
Vulkacit-F	0.2 g. per liter*.....	0.17	42	0.44	39	0.34	42	0.42	43
Vulkacit Thiuram...	0.002 molar	0.23	42	0.49	44	0.48	39	—	—
Vulkacit-P	0.002 molar	0.15	15	0.42	14	0.41	13	0.42	12
Vulkacit-D	Could not be determined polarographically								
Vulkacit-1000	Could not be determined polarographically								

* With this accelerator the molarity was indeterminate because the molecular weight was not known.

EXPERIMENTAL RESULTS

The investigation was first of all directed to accelerators which contain the mercapto group, *i.e.*, which are derived from 2-mercaptobenzothiazole, for these accelerators are among the most widely used in the rubber industry. The primary compound of this group, 2-mercaptobenzothiazole, is itself an important accelerator, put out by the I.G. Farbenindustrie under the name of Vulkacit Mercapto. The polarographic-potential diagrams obtained with it are reproduced in Figure 1.

In all four ranges of pH values, well defined steps were obtained. The depolarization potential values show the same characteristics as those of other substances already described. In acid solution reduction takes place more rapidly than in neutral solution or alkaline solution, as is evident from the data shown in Table I.

The values of the potential (DP) represent values obtained directly from the polarographs, without taking into account the anode potentials, which, in this particular analytical investigation, were of no significance. The heights of the steps (h) are based on the maximum sensitivity (approximately 2×10^{-9} ampere per mm. per m.).

To determine the content of 2-mercaptobenzothiazole in a rubber mixture, it is best to use a hydrochloric acid solution, since in this case, the polarographic step is particularly well defined, and since the height of the step is somewhat higher than with alkaline solutions and with neutral solutions.

The accelerator Vulkacit-AZ, which is closely related to 2-mercaptobenzothiazole, in that it is a reaction product of the latter and diethylamine, is used extensively in the German rubber industry because of the outstandingly good results which it gives in Buna mixtures. In addition to this, this accelerator gives well defined polarographic steps in all four pH ranges. Especially noteworthy is the simultaneous appearance of two steps in the case of acid solutions, which are well adapted to determining the accelerator content of a rubber mixture. The polarographs obtained with Vulkacit-AZ have already been published elsewhere[9]; the values derived from these polarographs are shown in Table I.

In view of the results obtained with 2-mercaptobenzothiazole, it was expected that its disulfide, *viz.*, benzothiazyl disulfide (Vulkacit-DM), would give similar values, and probably also considerably higher steps, since two reducible groups are present in this disulfide. This assumption was fully confirmed by the experimental results (see Table I). The depolarization potentials differ very little from those of Vulkacit Mercapto. For the same concentrations, the heights of the steps are more than six times as great as the height of the step of 2-mercaptobenzothiazole. This is an interesting phenomenon, but it will not be discussed further in the present paper.

Judged by the polarographic curves, which are not reproduced here because they differ only slightly from those of Vulkacit Mercapto, a hydrochloric acid solution is the most suitable one for determining the content of Vulkacit-DM in rubber mixtures.

Another accelerator, containing a mercapto group, which is used as the universal accelerator in many rubber factories, is Vulkacit-F, which is a combination of benzothiazyl disulfide with basic accelerators, and an accessory ingredient which improves its dispersion in a rubber mixture. In this accelerator, only the benzothiazyl disulfide component is polarographically active. It is not surprising, therefore, that the polarographic curves and data obtained with Vulkacit-F agree in almost every way with those obtained with Vulkacit-DM.

The polarographic properties of tetramethylthiuram disulfide and the piperidine salt of pentamethylene dithiocarbamic acid—two accelerators which do not contain the mercapto group—are of particular interest. Tetramethylthiuram disulfide (Vulkacit Thiuram) gives a polarograph of the kind shown in Figure 2. Of particular significance is the fact that, with sodium hydroxide solution, this accelerator does not give a polarographic step from which the accelerator can be evaluated. The values obtained with other electrolytes are recorded in Table I. A neutral solution gives the best results in quantitative determinations, and it has the advantage over hydrochloric acid, which also can be used for the same purpose, of giving a somewhat steeper polarographic step.

An attempt was made to identify by the polarographic method, in a natural rubber vulcanizate accelerated by tetramethylthiuram disulfide, the accelerator or any of its decomposition products which might remain after vulcanization.

A description of these experiments and of similar experiments with other accelerators may be found in detail in a paper by the author, to which reference has already been made[8].

The piperidine salt of pentamethylene dithiocarbamic acid (Vulkacit-P) gave the polarograph shown in Figure 3, and the values given in Table I.

In contrast to the accelerators examined previously, there were obtained, side by side, with neutral and alkaline solutions, two steps which it seems impossible to attribute to the phenomenon observed with numerous organic compounds, *viz.*,

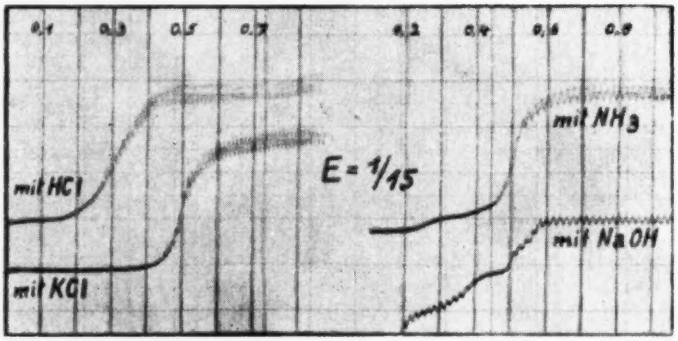

FIG. 2.—Polarograph of tetramethylthiuram disulfide in acid, neutral and alkaline solutions.

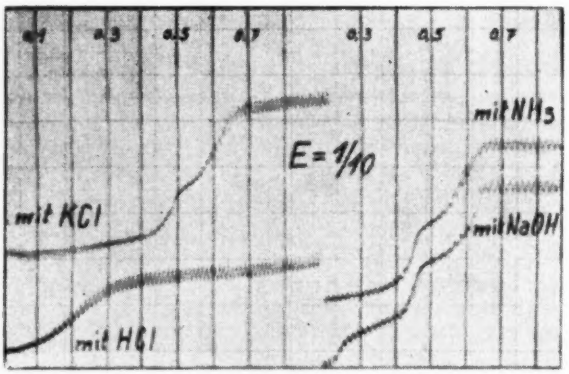

FIG. 3.—Polarograph of piperidinium pentamethylene-dithiocarbamate in acid, neutral and alkaline solutions.

that two steps appear side by side in the pH range of approximately 4 to 6. A neutral or ammoniacal solution is suitable for a quantitative determination. In measuring the height of the polarographic step, both steps are taken into account.

Finally, two basic accelerators—diphenylguanidine (Vulkacit-D) and *o*-tolylbiguanide (Vulkacit-1000)—were examined. For the reasons already cited at the beginning, these accelerators cannot be determined by the polarographic method.

CONCLUDING REMARKS

In the course of the present investigation, it was proved that the predicted polarographic properties of the vulcanization accelerators which were examined

were in substantial agreement with those of the compounds examined previously. The depolarization potentials obtained in neutral solutions are shown in Table II.

Table II shows, in addition, that even compounds such as tetramethylthiuram disulfide and the piperidine salt of pentamethylenedithiocarbamic acid have the same depolarization potentials as accelerators containing the mercapto groups, in spite of the fact that their molecular structures are considerably different. As far as the reducible part of the molecule is concerned, the differences lie only in the location of the double bond, as is evident from the position of this part of the molecules of 2-mercaptobenzothiazole and benzothiazyl disulfide on the one hand (**I**) and of piperidinium pentamethylenedithiocarbamate on the other hand (**II**):

There is no doubt that all organic compounds which contain either group **I** or group **II** can be determined by the polarographic method, provided it is possible

TABLE II

DEPOLARIZATION POTENTIALS OF ORGANIC COMPOUNDS WITH SIMILARLY REDUCIBLE ATOMIC GROUPS IN NEUTRAL SOLUTION

Compound	Volt
Azobenzene	0.2
Dimethylquinoxaline	0.7
Mercaptobenzothiazole	0.4
Benzothiazyl disulfide	0.4
Tetramethylthiuram disulfide	0.4
Piperidinium pentamethylenedithiocarbamate (1)	0.4
Piperidinium pentamethylenedithiocarbamate (2)	0.6

to prepare from the substance a solution which is suitable for polarographic measurement.

The results which have already been obtained seem to assure a new sort of application for the polarographic method, even if they do actually represent only a first step into a wholly new field. Further systematic studies will be necessary before all possible applications in the complicated subject of vulcanization accelerators is exhausted. Investigations which are concerned with the identification of accelerators in vulcanized rubber are of particular importance in this respect.

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INVESTIGATIONS OF RUBBER FILLERS

I. PARTICLE SIZE AND CHARACTERISTIC FORM OF CARBON BLACKS AND THEIR INFLUENCE ON THE PROPERTIES OF RUBBER MIXTURES, AS JUDGED BY ULTRA-MICROSCOPIC PHOTOGRAPHS *

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Fillers such as whiting, magnesium carbonate, zinc oxide and, above all, carbon black, which were originally added to rubber as diluents for the sake of economy, improve the physical properties of the products containing them to such an extent that they have today become of almost as much importance as the rubber component itself[1]. Although even today the cause of this activity has not been fully explained, investigations during the last ten years[2] lead to the conclusion that the activity shown by these fillers depends on:

(1) The affinity of the filler for the rubber, or the adhesion of the rubber molecules to the surfaces of the individual filler particles.
(2) The size of the particles.
(3) The shape of the particles.

The influence of the particle size and particle shape of fillers on the properties of rubber has been studied by numerous investigators with the help of every method suitable for the purpose[3]. These investigations have, however, given only average values, like those obtained by Behre[4] in a recent ultramicroscopic investigation, and are insufficient to warrant drawing any quantitative conclusions.

It is, on the contrary, possible by means of the electron microscopic method[5] to obtain an exact knowledge of the shape of primary carbon black particles, as has already been demonstrated in preliminary experiments by Beischer and von Ardenne[6]. The results obtained in their experiments made it appear essential to correlate these results in a more general way with the physical properties of rubber mixtures containing the blacks. With this in view, eighteen carbon blacks, placed at our disposal by J. Behre, were examined by the electron microscopic method. The physical properties of vulcanized rubber samples prepared from these blacks were measured by J. Behre, who has already described the methods used in making such measurements[8].

The electron microscopic photographs were taken with an apparatus developed by Siemens[9]. The carbon blacks, in an aerocolloidal state, were dusted onto collodion films. The evaluation of the photographs according to particle size was done statistically in the conventional way[6, 10].

In almost all cases the primary particles had the forms of hexagonal or circular platelets, the thickness of which it was possible to determine by stereoscopic photographs. Since, however, the thickness of the particles did not vary to any great extent, it was disregarded for the time being, and the diameter of the platelets was accepted as a basic measure of the particle size.

* Translated for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk*, Vol. 17, No. 1, pages 1-7, January 1941.

The discrepancy between particle sizes, as determined by the electron microscopic method and by x-rays, which was observed by Brill[11] and also by Biastok and Hofmann[12], was confirmed by the present authors. This difference is

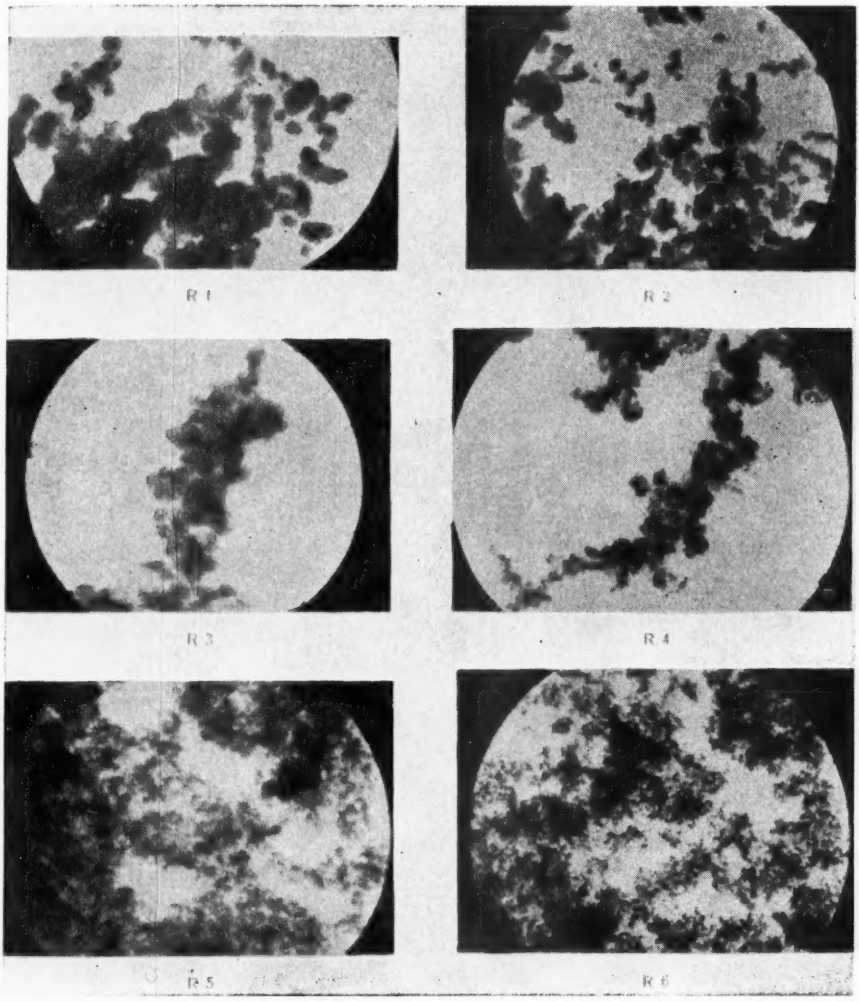

FIG. 1.

probably a measure of the mosaic structure in the lattice of the individual carbon black particles. This subject will not be discussed further at this time.

As already mentioned, the shapes of the particles vary from angular, hexagonal platelets to virtually round discs. The formation of a hexagonal structure is naturally a function of the conditions prevailing during preparation of the black, and round particles should be regarded as badly developed individual crystals.

Obviously the extent to which the characteristic form is developed influences to a certain extent the properties of a carbon black. Although an accurate determination of this "form factor" is hardly possible, the present authors chose the following method as a means of estimating this factor.

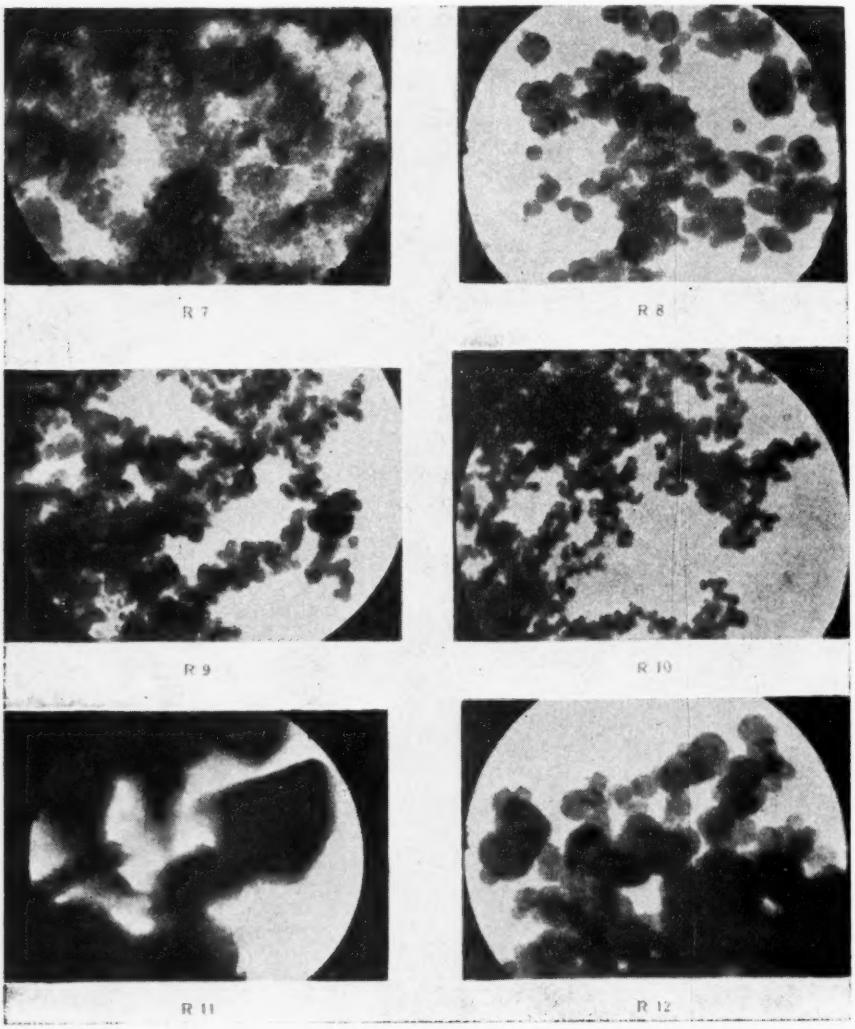

FIG. 2.

In the case of black No. 17, almost all the particles were characterized by angles and edges. This black was given a rating of 100 as a measure of the development of a characteristic form. Black No. 3, all the particles of which were round, was given a rating of 0. All the other blacks were evaluated on this basis, and were classified in a series, of which black No. 17 and black No. 3 were the extreme members. Evaluations by three independent observers, who only

rarely differed more than 20 per cent, were averaged. It is possible that a comparison of the particle size, measured by the electron microscopic method, with that measured by x-rays would give an accurate measure of the characteristic shape of the particle. The difference between these two values becomes

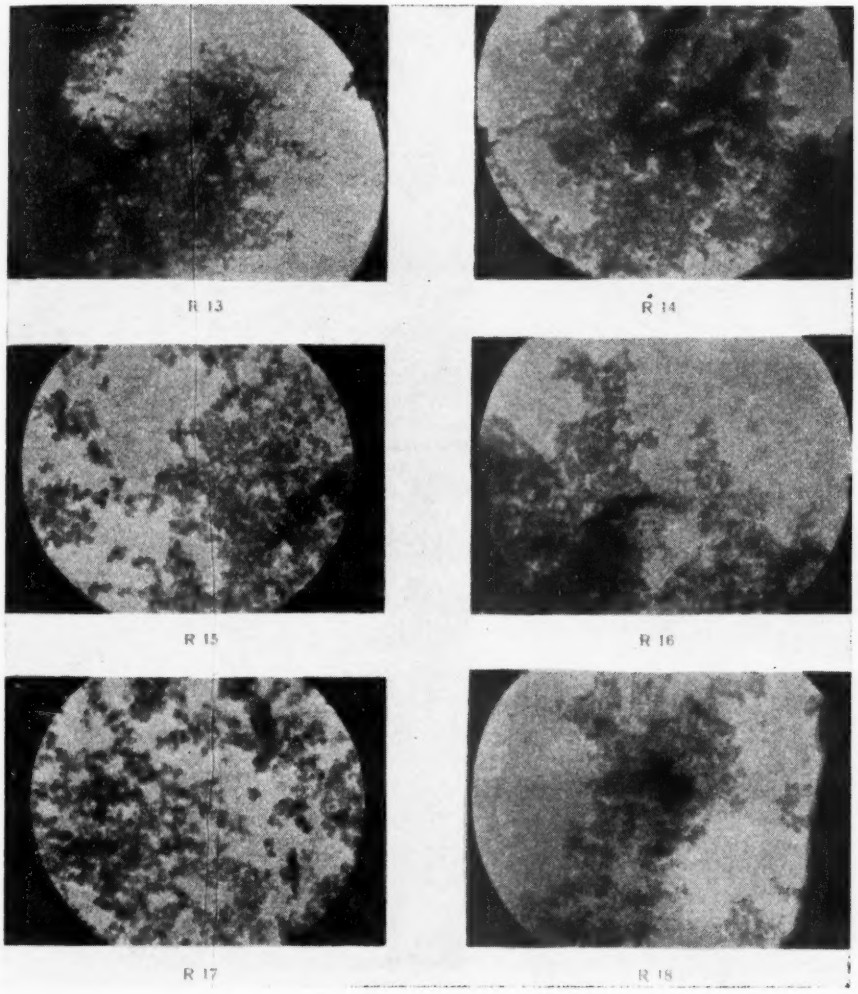

FIG. 3.

smaller with development of the characteristic form, since the latter is, in the last analysis, only a function of the increasing ordered state in the lattice[14].

Figures 1 to 3 (photographs R 1 to R 18) show a representative series of characteristic pictures of all the blacks which were examined. In Figure 4, distribution curves of particle size, derived from Figures 1 to 3 and from similar photographs, are shown.

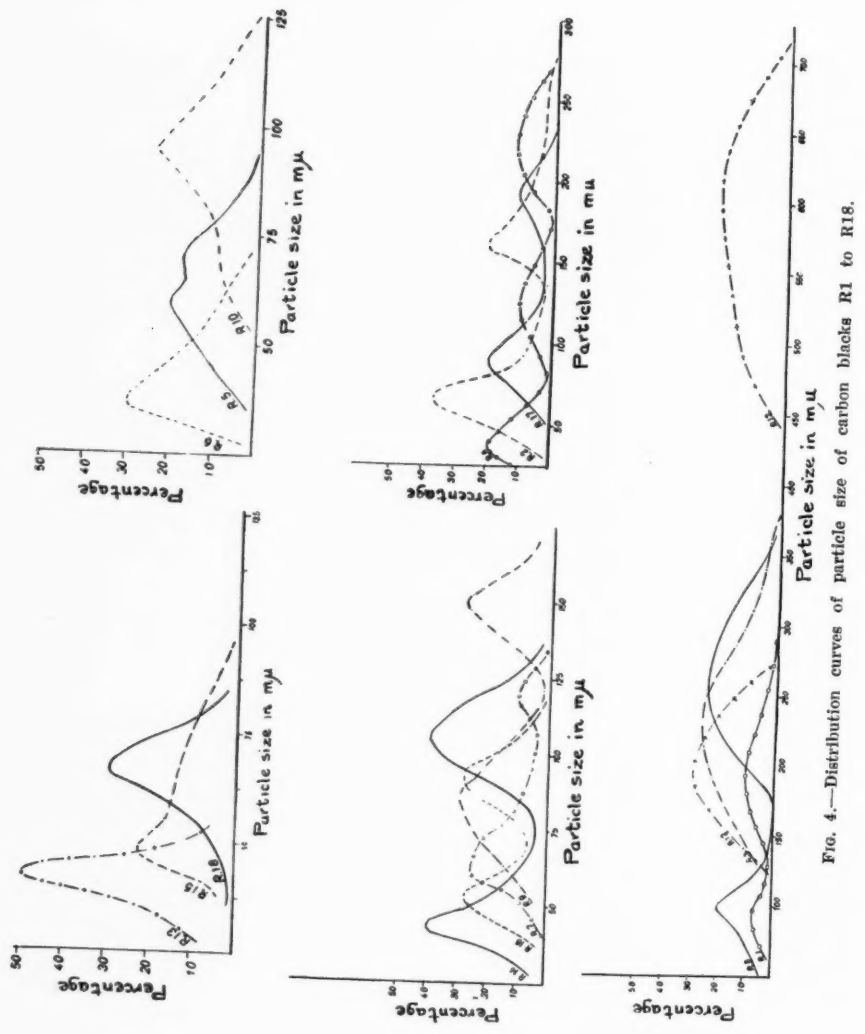

FIG. 4.—Distribution curves of particle size of carbon blacks *R1* to R18.

DISCUSSION OF THE RESULTS

The results which were obtained in the electron microscopic investigation described in the present paper are recorded in detail in the following summary. In this, the blacks are rated according to the development of a characteristic form, as described above for black No. 17 and black No. 3, in other words, the more highly developed the angular form and the fewer the round particles of a black, the higher the number assigned to it.

Carbon blacks have an influence on the tensile strength, resistance to tearing, elasticity, hardness, extensibility and stiffness of rubber mixtures prepared from them. The following tabulation contains all the measurements which were made of the eighteen blacks examined. There remained the problem of correlating in some way the physical properties of rubber mixtures with the particle size and shape of

Black No. 1. Coarse and irregular. Rating 30.
2. Very irregular. Rating 50.
3. Coarse. Particle-size distribution curve deviates from the mean value of 230 more than $\pm$ 100 mμ so the black must be classified as rather irregular. Rating 0.
4. Very irregular. Three components. Rating 85.
5. Fine and uniform. Rating 55.
6. Very fine and very uniform. Rating 60.
7. Fine and to a great extent uniform. Rating 15.
8. Coarse and irregular. Rating 15.
9. Fairly coarse and irregular. Rating 25.
10. Fine and uniform. Rating 50.
11. Coarse particles of coal, not comparable with the other blacks. Particle size around mμ. Could not be given a rating for shape of particle. In the graphic representation, it is given a rating of 0.
12. Very coarse and very irregular. Rating 20.
13. Fine and very uniform. Rating 40.
14. Irregular. Chief component approximately 70 per cent, and very fine. Rating 40.
15. Fine and uniform. Rating 80.
16. Fine and uniform. Two components. The finest and coarsest components deviate from the mean value by less than $\pm$ 100 mμ. Rating 65.
17. Similar to black No. 16. Uniform. The proportion of the second component is only 10 per cent. Rating 100.
18. Fine and uniform. Rating 50.

the blacks in these mixtures. This could naturally be done only by comparing similar types of blacks; in fact it was necessary to separate those blacks which had only a moderately fine particle size from those which contained particles of two or more different sizes.

Under these conditions, the surprising result was obtained that the maximum extensibility steadily decreased, and the stiffness steadily increased, with increase in the development of the characteristic shape. These relations were found to be true both of the blacks with uniform particles and of the blacks with irregular particles. The values were in all cases poorer for the blacks of irregular shape than for those with uniform particles (see Figures 5 and 6). It is possible that in this case the particle size plays a secondary rôle, although the influence of the particle size is not at all evident.

With sixteen of the eighteen blacks, the stiffness of the rubber mixtures depended on the proportion of characteristically shaped particles. Only blacks Nos. 1 and 11 were exceptions. Likewise the extensibility depended on the

proportion of characteristically shaped particles, except for blacks No. 4, No. 11 and No. 14. Black No. 11 should not be regarded as a black at all, at least as far as the present work is concerned. Black No. 1 was a lamp black, and it may be assumed that residues from the source material influenced in an uncontrolled way the physical properties. Black No. 4 and Black No. 14 had particles of different shapes and, as far as extensibility is concerned, the vulcanizates con-

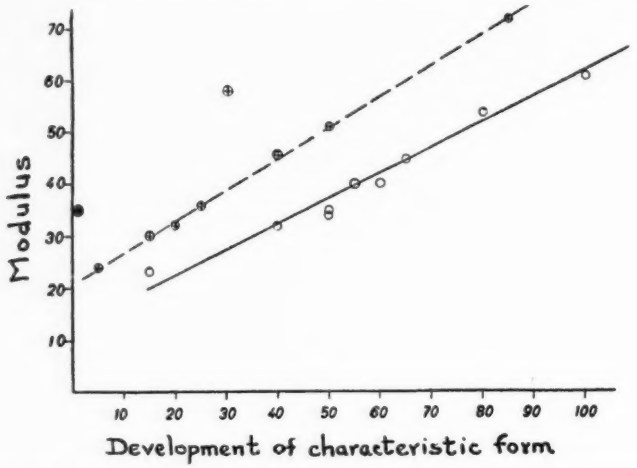

FIG. 5.—Stress at 200 per cent elongation as a function of the development of a characteristic form.

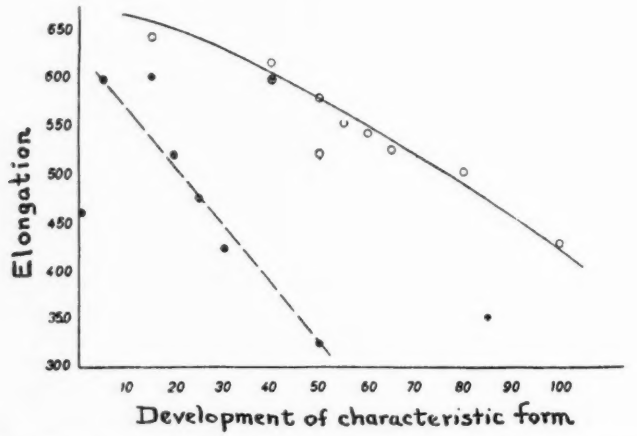

FIG. 6.—Maximum elongation as a function of the development of a characteristic form.

taining these blacks were of better quality than vulcanizates containing the other blacks of irregular particle size. At the present time no explanation of this can be offered.

Simple and definite relations of a similar kind could not be found for the other physical properties. When it is attempted to represent the tear resistance as a function of the mean particle size (the mean particle size of the component in highest proportion in the case of blacks having particles of different sizes), a

curve like that shown in Figure 7 is obtained. It may be said, in a qualitative way, that the resistance to tearing was above 100 for particle sizes below 80 mμ. However, a functional relation could not be derived from the widely varying values and, in any case, it is obvious that the influence of particle size cannot be anywhere nearly so great as has been assumed heretofore[15]. This is quite evident by the data in Figure 1. Only with particle sizes of approximately 200 mμ, or larger, does the influence of particle size become evident in all cases. Tensile strength, hardness and elasticity appear to be complex functions of the differential surface properties of the blacks. As a matter of fact a marked lack of uniformity of particle size appears to be characterized by a relatively low activity of the black.

The preliminary experiments described in the present paper show that it is now possible to judge the value of a black, insofar as the stiffness and extensibility and, in a rough way, the tear resistance as well, which it imparts to rubber are

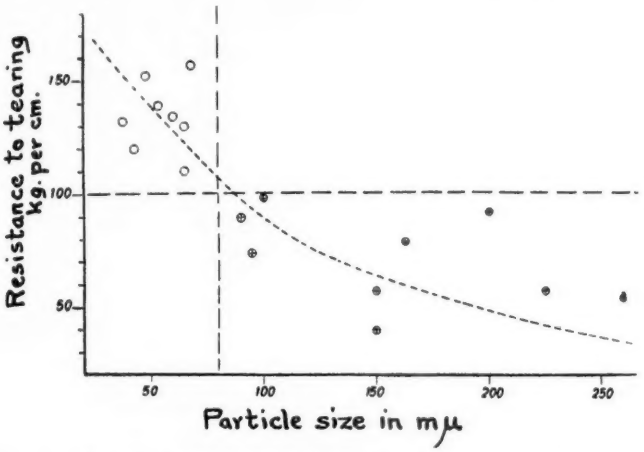

FIG. 7.—Influence of particle size on resistance to tearing.

concerned, by electron microscopic examination. In continuing the work, it will be necessary, first of all, to explain the mechanism of the action of fillers. When this is done, it will probably be possible to derive a functional relation between physical properties, particularly tensile strength and elasticity, and the structure of the filler particles.

SUMMARY

The particle sizes and characteristic shapes of the particles of eighteen blacks used in the rubber industry were determined. The values which were obtained are compared with the physical properties of rubber mixtures prepared from these blacks. The characteristic shape of the particles has the greatest effect on the extensibility and the rigidity at 200 per cent elongation, *i.e.*, on the modulus.

When the particle size of a black is over 100 mμ, relatively poor resistance to tearing of vulcanizates containing the black is obtained.

In general, the particle size of a black has far less influence on the other physical properties than has been believed in the past. With the aid of electron microscopic photographs, it is possible to estimate the value of a black as a filler in rubber.

ACKNOWLEDGMENT

The authors wish to thank Professor P. A. Thiessen for his interest and assistance in this investigation, and the Deutsche Forschungsgemeinshaft for the aid given in supplying the apparatus. Also thanks are due J. Behre for his continued help.

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GASOLINE DIFFUSION RESISTANCE OF THIOKOL TYPE F*

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The solvent-resistant properties and low swelling characteristics of Thiokol[1] synthetic rubbers are well known to the rubber technologist. It is also known that these rubbers are highly resistant to permeation by solvents. Gasoline and blends of gasoline and benzene do not diffuse into and through them to any great extent.

The permeation of rubber and synthetic rubbers by fixed gases, such as hydrogen and helium, has been the subject of considerable study. Such information has a bearing on the construction of dirigibles, blimps, observation balloons, and barrage balloons. Sager[2] shows that the ratio of permeability to hydrogen for Thiokol Type DX (now Type F), compared to rubber at 25° F, is 1 to 12.

Recently the diffusion of gasoline and oil through solvent-resisting synthetic rubbers has become of general interest. The information generally sought is the amount of gasoline that diffuses through a given area in a given time.

DIFFUSION TEST METHODS

Since losses are expressed in terms of unit area, the total area of the test-piece is of little importance, except to the extent that it affects the accuracy of the weighings or measurements. A simple apparatus that has been found satisfactory for use with cured sheets is made from a screw-cap Mason fruit jar, equipped with a Kerr screw cap. The metal disk in the top of the cap is removed. In its place is inserted a disk cut from 16-mesh wire screening and a disk cut from the piece of rubber to be tested. The jar is filled with the desired amount of gasoline, the cap assembly screwed on, and the jar weighed. The jar is hung, or suspended in, an inverted position in a constant-temperature room, and is weighed at intervals. The wire screening serves to protect the test-piece from sagging or stretching under the weight of the gasoline.

Where weighings are to be made on an analytical balance, the fruit jar may be too large. A similar container can be made from a six-ounce wide mouth bottle equipped with a metal screw cap. The center of the cap can be cut out. This leaves a ring with an opening $1\frac{3}{4}$ inches in diameter. This ring, when fitted with the wire disk and test-piece, can be screwed on the bottle to make a tight seal. Where coated fabrics are tested, it may be necessary to bolt the test-pieces between metal flanges attached to a metal cup.

The data shown in this report were obtained with both types of apparatus. The jars were used for cured sheets, and metal cups with flanges for testing coated fabrics. In measuring diffusion losses, 150 cubic centimeters of liquid were put in the apparatus; this was hung in a constant temperature room at 75 to 78° F, and weighed at intervals on a scale accurate to 0.02 gram. Weights were recorded to the nearest 0.1 gram. All measurements were made in triplicate, and averaged.

Tests have indicated that the volume of gasoline per unit of area can be varied widely without affecting the diffusion rate. In cases where the diffusion is so high

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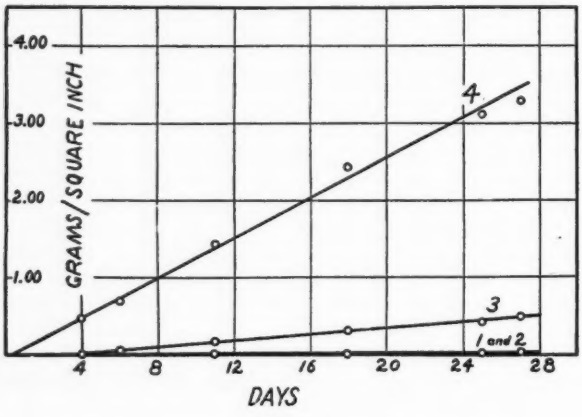
that it changes the composition of the gasoline by loss of the more diffusible components, the rate may be affected. The data in some cases show zero diffusion. This means that the loss in weight of the container was so slight that it could not be detected under the conditions of the experiment.

DIFFUSION TESTS ON SHEETS

As can be seen from the data given here, the diffusion of gasoline, and of gasoline containing appreciable amounts of aromatics, through Thiokol Type F is exceedingly low. The formula of the Thiokol Type F stock was selected as representative of compounds in regular factory production.

To obtain certain special characteristics, it may be desirable to blend Thiokol Type F with other synthetic rubbers.

Data on the diffusion of gasoline through a few such blends, along with the diffusion data for the Thiokol Type F stock, are shown. Although the data are



Stocks

1. Stock No. 1 Thiokol F
2. Stock No. 2
3. Stock No. 3
4. Stock No. 4

FIG. 1.—Diffusing 73-octane aviation gasoline through Stocks Nos. 1 to 4—sheets 0.062-inch thick; temperature 75° F.

for blends of Thiokol Type F, with any one other type of synthetic rubber, laboratory tests indicate that the principle of blending to obtain special characteristics can be applied to the other oil-resisting synthetic rubbers without materially increasing diffusion.

The data given here were obtained on the following:

Stock No. 1—A Thiokol Type F compound.

Stock No. 2—A blend consisting of 100 parts of Thiokol Type F and 20 parts of another synthetic rubber (by weight of Thiokol F).

Stock No. 3—A blend consisting of 100 parts of Thiokol Type F and 60 parts of the other synthetic rubber.

Stock No. 4—A stock solely of the synthetic rubber used for blending with the Thiokol Type F in stocks Nos. 2 and 3. This synthetic rubber stock was a conventional type of compound, but may or may not be typical of this particular synthetic rubber for low permeability.

In Figure 1 is plotted the diffusion of a commercial grade of 73-octane nonleaded aviation gasoline through these stocks.

Similar data obtained with a number of different aviation gasolines show approximately the same differences between stocks, but the actual rates vary with different gasolines. This is, no doubt, due to variations in composition of the gasolines, especially their aromatic contents.

The cumulative diffusion losses of a 100-octane leaded aviation gasoline through these same stocks are shown in Table I. The tests were run at 75° F, and the losses are expressed as grams per square inch.

When compared with those in Figure 1, the above data show that 100-octane gasoline does not diffuse through certain of these stocks so rapidly as does 73-octane gasoline. High-octane aviation fuels contain a minimum of aromatics, and this probably accounts for the difference in behavior of the two gasolines. Although neither fuel was checked for its aromatic content, the 73-octane gasoline was in no sense a high aromatic fuel.

TABLE I

TOTAL DIFFUSION LOSS

Stock No.	Sheet thickness (inch)	Time in days							
		1	2	4	6	8	10	12	14
1	0.062	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01
2	0.062	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01
3	0.062	0.01	0.01	0.02	0.02	0.02	0.02	0.04	0.04
4	0.062	0.00	0.01	0.15	0.27	0.37	0.47	0.60	0.70

Since it is possible that aviation fuels may be blended with aromatics, these same stocks have been tested in a blend made up as follows:

Aromatic blend	Percentage
73-Octane aviation gasoline	70
Benzene	10
Toluene	10
Xylene	10

The diffusion of this blended gasoline through the series of stocks is shown in Figure 2, which illustrates the following points:

1. Diffusion of gasoline through the blends is not proportional to the volume ratio of the crude synthetic rubbers used in the blends. For example, stock No. 2, which is a 100: 20 blend, shows exceedingly low permeability.

2. The Thiokol Type F stock is practically impermeable to straight aviation gasoline and to the aromatic blend.

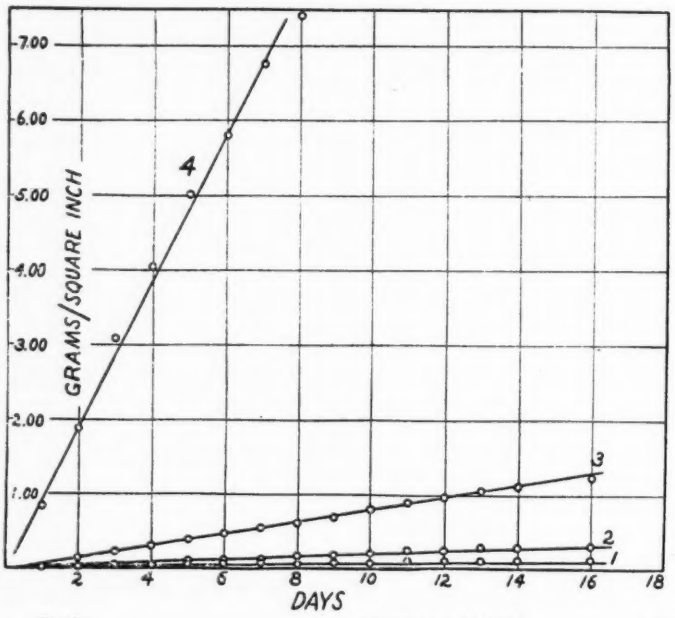
The data shown in Figures 1 and 2 and in Table I were all obtained with sheets approximately 0.062-inch thick. As thickness is another variable which has an effect on rates of diffusion, sheets of different thicknesses were tested, using 73-octane aviation gasoline. The cumulative losses of gasoline through the various sheets are shown in Table II. The tests were run at 75° F, and the losses are expressed in grams per square inch.

Further data on the low diffusion of gasoline through relatively thin layers of Thiokol Type F are given in the section dealing with the diffusion through coated fabrics.

DIFFUSION TESTS ON COATED FABRICS

The data above were obtained with sheets of the synthetic rubber stocks. The combinations of Thiokol Type F with the other synthetic rubber were obtained by blending during mixing. Other combinations of synthetic rubbers are possible through the separate layers used on impregnated and coated fabrics. Comparative tests for permeability were made on two-ply fabric, with an inner layer and a coating on each outer surface. The coated fabrics tested were:

Test A— Coated with Thiokol Type F stock throughout.
Test B—Coated with another synthetic rubber throughout.



Stocks	Composition of blend	Percentage
1. Stock No. 1 Thiokol F	73-Octane Aviation Gasoline	70
2. Stock No. 2	Benzene	10
3. Stock No. 3	Toluene	10
4. Stock No. 4	Xylene	10

FIG. 2.—Diffusion aromatic blend through stocks Nos. 1 to 4—sheets 0.062-inch thick; temperature 75° F.

TABLE II

TOTAL DIFFUSION LOSS

Stock No.	Sheet thickness (inch)	Time in days					
		3	5	7	12	14	18
1.....	0.032	0.00	0.00	0.00	0.00	0.02	—
	0.062	0.00	0.00	0.00	0.00	0.00	0.00
2.....	0.029	0.02	0.02	0.05	0.08	0.11	—
	0.062	0.00	0.00	0.00	0.00	0.00	0.00
3.....	0.032	0.05	0.09	0.14	0.24	0.29	—
	0.062	0.00	0.04	0.07	0.19	0.21	0.30
4.....	0.031	0.54	0.93	1.38	2.38	2.72	3.58
	0.048	0.33	0.62	0.92	1.62	1.87	2.46
	0.073	0.12	0.25	0.45	0.92	1.00	1.50
	0.134	0.02	0.16	0.31	0.71	0.88	1.18

Test C—The synthetic rubber between the plies was a Thiokol Type F stock. The outside surfaces were coated with another type of synthetic rubber.

The cumulative diffusions of 73-octane aviation gasoline through these fabrics, over a 14-day period, are shown in Table III.

These samples were taken from commercial runs, and the exact compositions of the synthetic rubber stocks were not revealed. The total thickness in all cases

TABLE III

TOTAL DIFFUSION LOSS

(Grams Per Sq. In.)

Type	Time in days		
	1	7	14
A	0.00	0.02	0.03
B	0.45	3.08	5.35
C	0.01	0.03	0.06

was 0.016-inch. In Test C, the Thiokol Type F stock represented a high percentage by weight of the synthetic rubber stocks used. The diffusions in Test A and in Test C are exceedingly low. It is interesting to note that the combination of synthetic rubber in Test C shows the same low diffusion of the Thiokol Type F stock between the plies.

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SOME PHYSICO-CHEMICAL PROPERTIES OF CARBON BLACKS *

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COLLABORATING IN THE WORK DESCRIBED WERE THE STUDENTS

V. Avgustin and A. Dobrovolski

The rubber industry of the U. S. S. R., which keeps on growing from year to year, has been using constantly increasing quantities of blacks, the quality of which must satisfy specifications that become constantly more severe. Little wonder, therefore, that numerous investigators are seeking to explain the reinforcing action of blacks in rubber mixtures, and to work out methods by which it will be possible to determine their activities quickly and easily. Research along these lines is proceeding mainly in the direction of determining the adsorptive powers of blacks with respect to various substances, and likewise of measuring the heats of wetting, the size of the particles, etc.

It is known that blacks have great surface areas, which in the case of certain types—active types—amount to 200 square meters per gram.

It would appear that the reinforcing properties of blacks depend primarily on their specific surface areas. Yet some types with very small particles (Superspectra) are less active in crude rubber than the blacks usually employed (Micronex type), the particles of which are several times larger.

The present article cannot go into all the work done in this connection. For example, the adsorption of various dyes, accelerators, iodine, acids and bases from water, alcohol or benzene solutions, has been studied[1].

The study made in the Lwow laboratory for petroleum research had for its object the determination of the adsorptive power of various types of blacks for the vapors of certain volatile organic liquids, in particular carbon tetrachloride[2].

When constant test conditions are maintained, this method gives uniform and repeatable results.

In an article by one of the present writers[2], the method of measurement is described, with data on various types of blacks.

In the present report data on the adsorptive powers of certain kinds of blacks with different concentrations of carbon tetrachloride vapor in air are submitted. A reliable criterion by which the activity of the blacks could be estimated rapidly was of special importance in connection with the catalytic process worked out by the present authors[3] for the activation of thermic blacks (which are by nature little active), since such a criterion would make it possible to control the progress of the activation process.

Table I shows the results obtained.

With these figures as a basis, Freundlich isotherms were calculated from their logarithmic coördinates; their form, however, is hardly characteristic, and does not make it possible to draw any general conclusions. A very characteristic difference is shown only in the figures for maximum adsorption power, given in Table II, which indicates the maximum percentage by weight of carbon tetra-

* Translated by Lewis Bertrand from *Kauchuk i Rezina*, Technical Section, No. 10, pages 14-16, October 1940.

chloride adsorbed at a concentration of 0.5840 gram of carbon tetrachloride (per liter of air).

Table II shows a perfectly marked division of blacks into active, characterized by high powers of adsorption, and inactive, with low powers of adsorption. The exception referred to above is Superspectra black, which, despite its very great adsorptive capacity, is less active in crude rubber than other blacks.

TABLE I

WEIGHT IN PERCENTAGE OF CARBON TETRACHLORIDE ADSORBED BY THE BLACK (AT 15° C)

Type of black	CCl_4 concentration (in g.) per liter of air			
	0.069	0.140	0.322	0.702
Thermax	0.33	0.48	0.70	1.1
Borislavsky A	1.00	1.25	1.67	2.5
Borislavsky B	1.15	1.70	2.50	4.0
P-33	0.84	1.30	1.93	3.4
Lampblack	0.70	1.06	2.00	3.8
Acetylene black	4.40	5.45	7.00	9.4
Gas Micronex	3.80	5.06	7.60	11.7
Gas Carbomet	4.30	6.40	9.00	13.8
Superspectra	27.50	32.10	41.10	63.5
Active carbon	52.00	57.30	60.7	65.7

TABLE II

Type of black	Percentage by weight of carbon tetrachloride adsorbed
A black of strong coloring power obtained by incomplete combustion of natural gas (Superspectra)	61.5
Active blacks obtained by incomplete combustion of natural gas:	
Micronex	10.5
Spheron	14.2
Kosmobile-66	14.3
Carbomet No. 3	11.0
Dixie	11.6
Arrow	13.2
Active black from naphthalene	12.2
Acetylene black	8.4
Thermic black, Thermax	0.83
Thermic black, P-33	2.44
Lampblacks:	
A	3.10
B	2.80
C	2.60
106 Vegelin	2.90

The heat of wetting of blacks moistened with carbon tetrachloride was investigated. As is known, there is a relation between maximum adsorption and heat of wetting. A study along these lines was undertaken by Hock and Boström[4]. The latter has published the results of his research on the heat of expansion for mixtures of crude rubber and blacks[5].

Hock[6] arrived at the conclusion that there is no connection between the heat of wetting of a black by benzene and the degree of blackness of the black.

In the present research, a Dewar flask was used as a calorimeter; the flask was placed in a thermostat, and at the bottom of the flask about 10 grams of test black was placed. Through the stopper with which the flask was sealed

were a glass mixer, a Beckmann thermometer and a pipette; the latter was closed at the bottom with a stopper and could be opened from without.

Before proceeding to measure the data, the heat content of the entire system was determined. It is essential that the temperature of the black, wetting liquid and entire system be uniform. Equalization of temperature in our apparatus was maintained for 3 to 4 hours. After complete uniformity of temperature was attained, the apparatus was opened from without by means of a specially adapted stopper, which sealed the pipette filled with the wetting liquid. The moistened black was then stirred with a glass mixer to obtain a uniform temperature throughout the mass. The measurement was continued about 3 minutes.

As a preliminary, a blank test was made to obtain a correction factor for the heat of evaporation of the liquid.

Use of a Beckmann thermometer was found indispensable because of a slight increase in temperature, which in our experiments amounted at the most to 3° C.

Carbon tetrachloride was used as the moistening liquid.

The results are given in Table III.

TABLE III

Type of black	Heat of wetting (cal. per g. of black)	Coefficient a
Thermax	0.1	0.09
Thermic Borislavsky A	0.2	0.08
P-33	0.3	0.088
Lampblack C	0.3	0.08
Acetylene black	0.7	0.075
Gas Micronex	1.1	0.09
Gas Carbomet No. 3	1.8	0.13
Gas Superspectra	6.5	0.098

From Table III a perfect parallel is evident between the maximum degree of adsorption (Table I, concentration of CCl_4=0.702 g. per l.) and the heat of wetting.

In consequence of very slight increases in temperature, these figures are not altogether accurate, so that the values for coefficient a (Table III) in the familiar equation $Q=aA$, which expresses the relationship between heat of wetting and maximum adsorptive capacity, are only approximate.

This is explained by the difference in structure of active lamp and thermic blacks. By this method, however, the degree of activity of a black can be approximately determined.

In addition, we determined the fat coefficients, based on absorption of linseed oil.

The results show that there is no evident relation between the fat coefficient and the effects of a black on crude rubber.

We likewise attempted to determine the temperatures of spontaneous combustion of various blacks in oxygen by means of the apparatus described by Swietoslawski, and Roga[7]. This method yielded results which are definitely reproducible.

The results show that there is a relation between the point of spontaneous combustion and adsorption capacity; in any case, on the basis of the point of ignition the conditions which characterized the formation of the black can be determined. Thus, blacks obtained in a reducing atmosphere possess the very highest ignition points; acetylene black, for example, ignites only at 535° C. In the case of thermic blacks, the points of ignition lie between 449 and 485° C.

Lamp blacks obtained in an oxygen atmosphere, but with only a weakly developed surface, have ignition points between 352 and 362° C.

Active blacks obtained by incomplete combustion of natural gas ignite at temperatures of 313 to 324° C.

A special group consists of blacks with high coloring powers and deep black shades, which have relatively low ignition points.

The ignition temperatures of the blacks do not depend so much on the development of their surfaces as on the method and temperature of obtaining the blacks. Apparently the presence of volatile matter definitely lowers the ignition point; its presence is a result of the oxidizing atmosphere in which a black is obtained.

From the data it is evident that blacks can be classified according to their points of ignition into:

1. Acetylene blacks
2. Thermic blacks
3. Lamp blacks
4. Active gas blacks
5. Blacks with strong coloring powers.

The presence of slight percentages of inorganic salts, such as sodium chloride, potassium carbonate, etc., lower appreciably the ignition points, in some instances to as low as 200° C.

A study was made also of the electrical conductivities of certain types of blacks. In this connection, it was assumed that thermic blacks, as they contain more graphite, would be better conductors of electricity than other types.

The data were obtained at 100 atmospheres' pressure at the Institute for Experimental Physics of the University of Lwow, by the improved Rishkevich method[8]. From the results obtained it was not possible to establish any relation between the electrical conductivity and degree of activity.

CONCLUSIONS

A study was made of the adsorption of carbon tetrachloride vapor by various types of blacks, and data were obtained on the heats of wetting of blacks by carbon tetrachloride.

A study was made of the fat coefficients and the points of spontaneous combustion of various types of blacks.

It was found that active blacks can be distinguished from inactive blacks by their powers of adsorption of carbon tetrachloride and also by their heats of wetting.

There is no way of telling by its fat coefficient whether a black is of value in rubber.

The point of spontaneous combustion gives an approximate idea of the origin and formation of a black.

Data on electrical conductivity have thus far not provided any basis for classifying different types of blacks.

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HYSTERESIS TESTS ON TIRE COMPOUNDS

J. G. MACKAY, J. G. ANDERSON and E. R. GARDNER

The authors of the paper with the title above, which was published in the April 1941 issue of RUBBER CHEMISTRY AND TECHNOLOGY, pages 421-432, have made the following three corrections of their paper in its original form in the *Transactions of the Institution of the Rubber Industry*.

(1) Table I on page 422:

The temperature rise after 25 minutes' flexing for the sample prepared by method (b) should read 103.5° F instead of 10.3° F.

(2) Table IX on page 428:

The temperature rise for the untreated stock at 60 minutes' cure should read 77° F instead of 70° F.

(3) The last paragraph on page 427:

The paragraph which reads: "A master batch of the following composition was mixed in an internal mixer for 6 minutes at a temperature of 310° F" is not fully explanatory, and should read: "A master batch of the following composition was used in an internal mixer at normal temperatures. When all of the black was incorporated, the temperature of the mix was raised to 310° F, and working was continued for 6 minutes."

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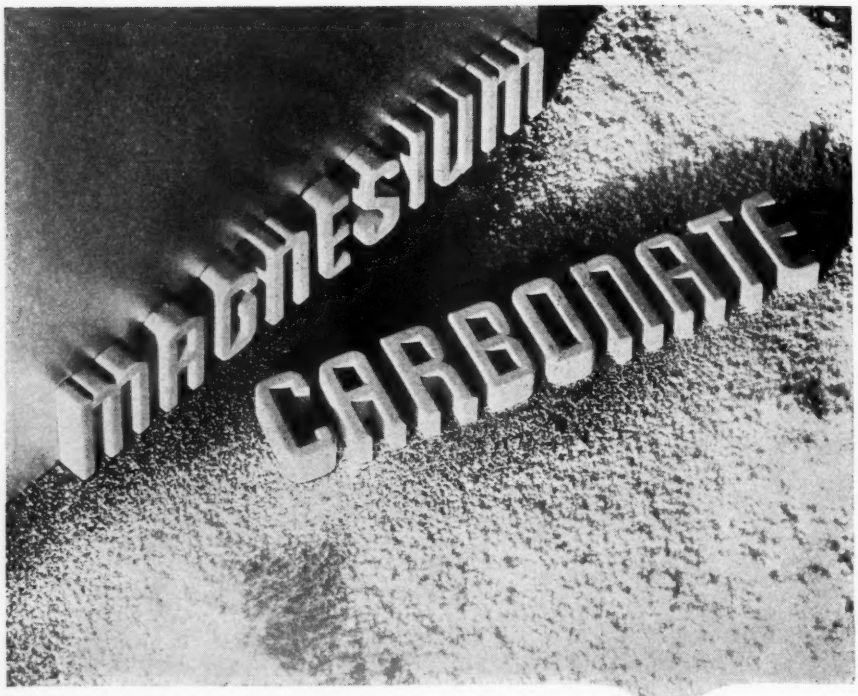

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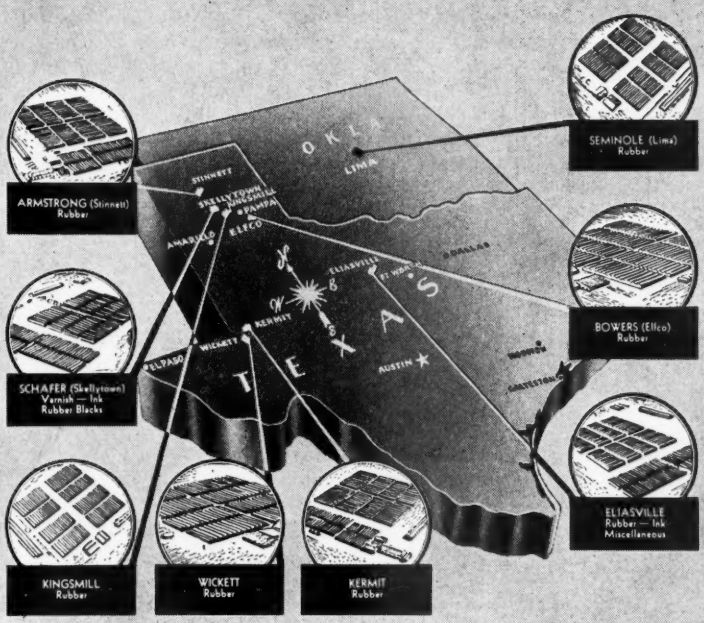

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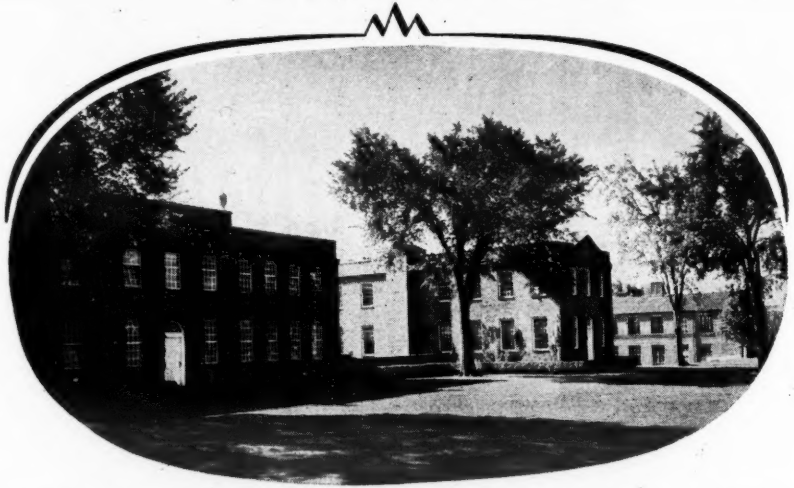

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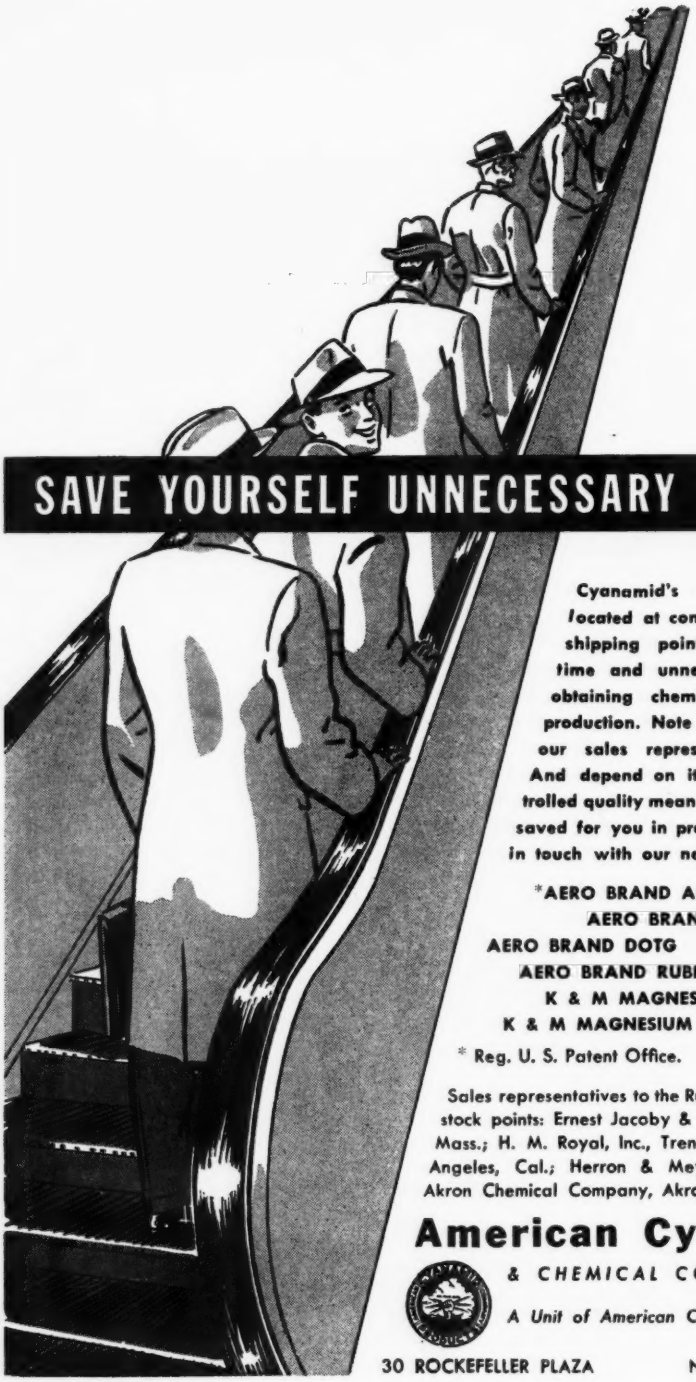

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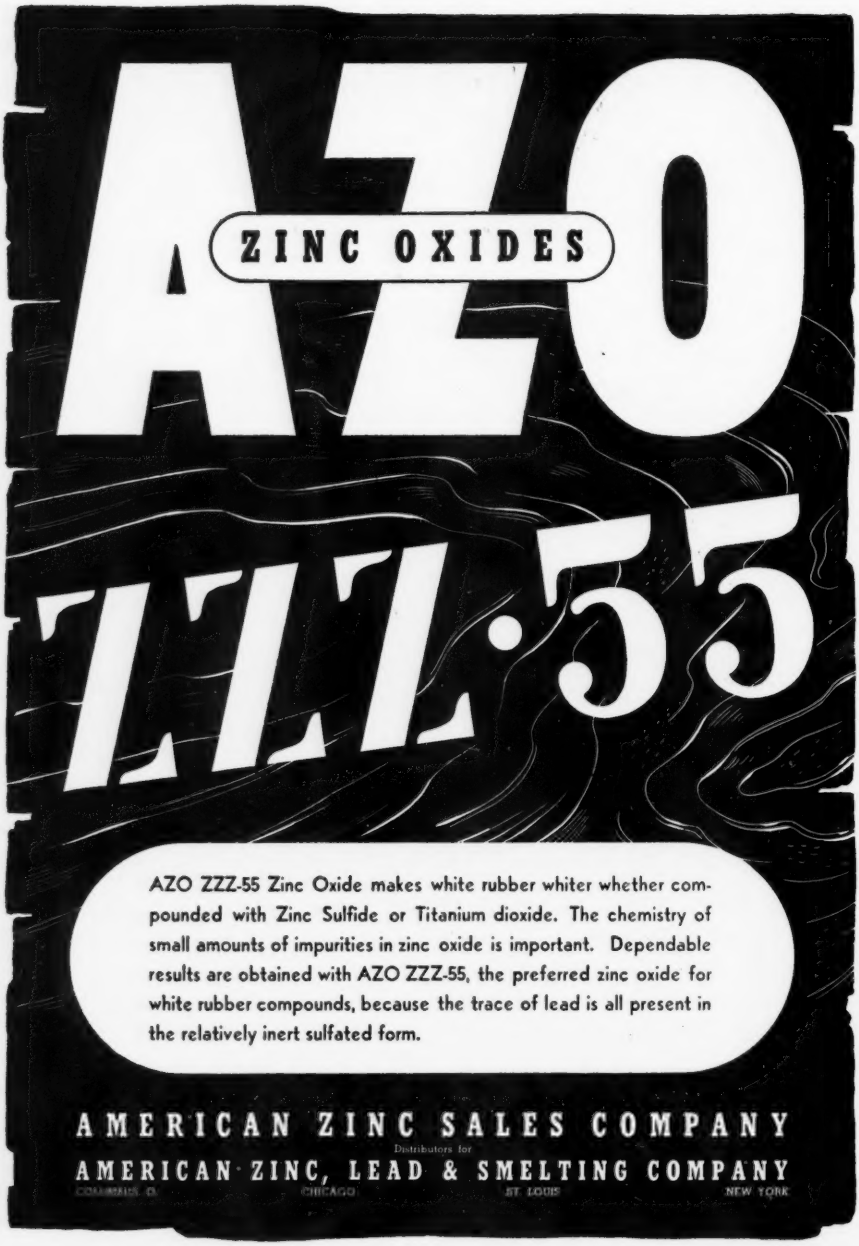
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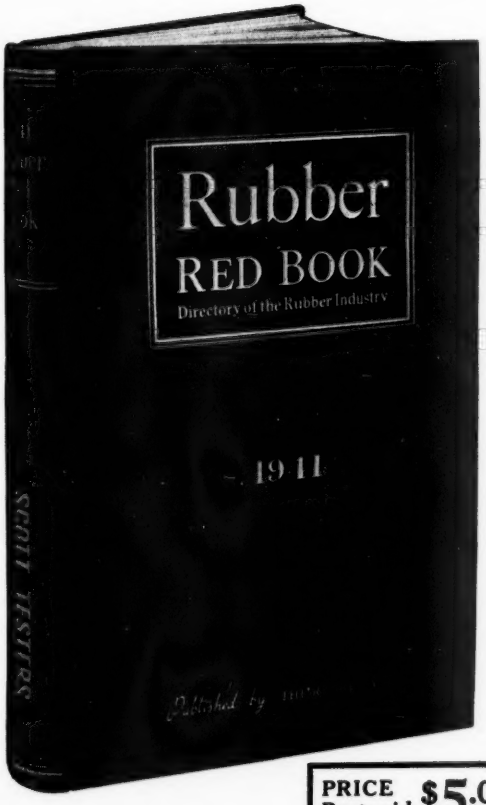

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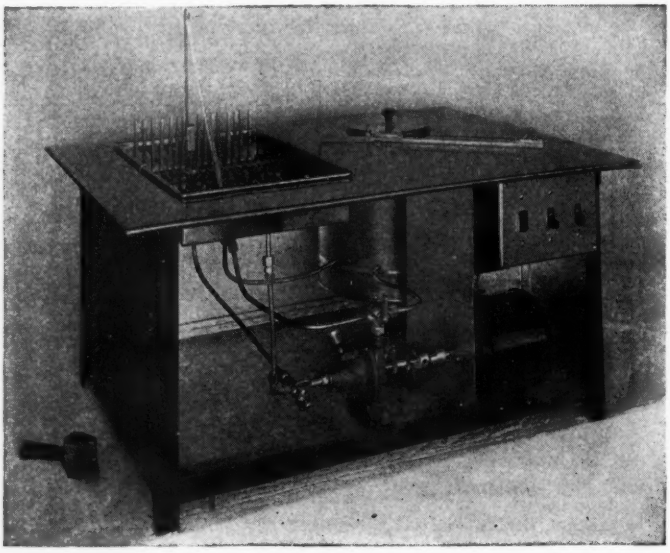

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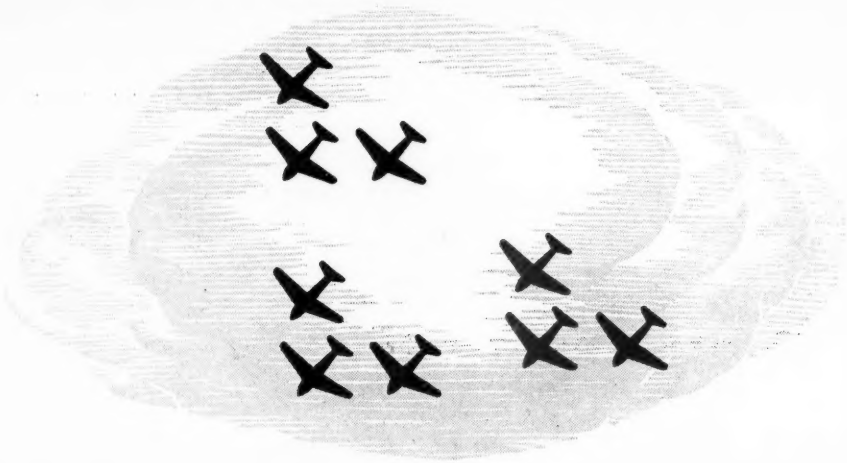

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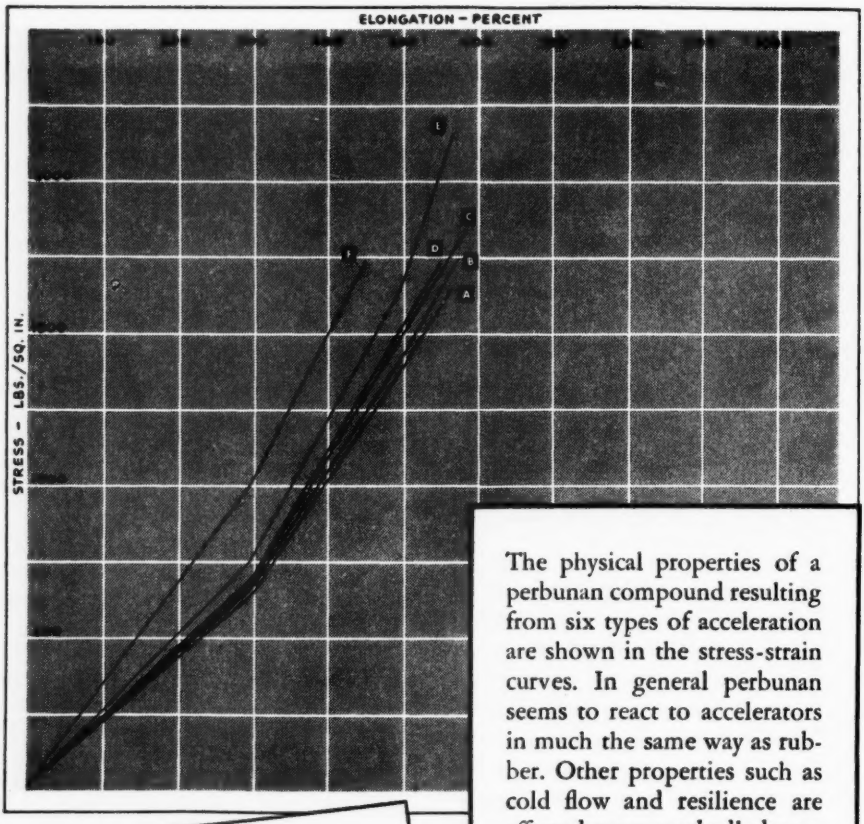

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Sulfur	1.5
Zinc Oxide	5.
Stearic Acid	1.
Dibutyl Phthalate	20.
Flectol H	2.
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